Narrowband CARS spectroscopy in the molecular fingerprint region

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Abstract

We demonstrate high-resolution narrowband coherent anti-Stokes Raman scattering (CARS) spectroscopy on several organic samples from 900 to 3600 cm⁻¹, covering a large part of the molecular fingerprint region. We use a magnesium oxide-doped periodically-poled lithium niobate-based (MgO:PPLN) optical parametric oscillator, with a novel variable output coupler, as a tunable laser light source. Its signal wavelength ranges from 880 to 1040 nm and its idler from 1090 to 1350 nm. We compare the CARS spectra thus obtained to spontaneous Raman spectra using a phase retrieval algorithm and find them in extremely good agreement. We test the effects of sample concentration and input pulse bandwidth on the coherent anti-Stokes Raman intensity. We also briefly investigate the vibrational dephasing of the O–H stretch vibration in water.

Cover photo: Martin Jurna

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Introduction

Interaction between light and matter is what makes life interesting. If light simply bounced off objects without interacting, there would be no colors, and we would not be able to see them if there were; there would be no windows, because glass would be opaque; and the daytime sky would be black, or perhaps gray.

Fortunately, light does interact with matter, and the physical laws governing this interaction have fascinated physicists for hundreds of years. The subject of this research is the influence of light on the vibrations of the molecules that make up the matter around us. Light can be understood as an electromagnetic wave that moves the charged particles present in atoms; a moving charge, in turn, creates an electromagnetic wave, and so the atoms influence the light. If the light is intense enough (for example, if it came from a laser) then all sorts of remarkable effects can be observed. This is called nonlinear optics.

Moving from vague analogies about how the universe works to the research at hand, we study molecular vibrations caused by light. These vibrations are important because the molecules of any given substance vibrate in exactly the same way; and differently from any other substance. Each vibration takes a certain amount of energy, and we can measure a molecule's vibrational response at different amounts of energy. If we draw a graph of this response as a function of the energy, it will look something like figure 1.1. That particular graph, or vibrational spectrum, is unique to polystyrene, a widely-used plastic; one can compare it to a fingerprint, uniquely identifying the presence of a molecule at a "crime scene."



Figure 1.1. The "fingerprint" of polystyrene, a widely-used plastic.

Continuing the crime scene metaphor, vibrational spectroscopy is a subject of interest to the "disease detectives" of the medical world. Certain diseases, such as Alzheimer's, or Creutzfeldt-Jakob disease, leave traces of certain proteins in the body, and studying these can secure us a diagnosis, or provide us with information on the progression of the disease, ultimately contributing to its cure.

We study these molecular vibrations using a nonlinear optical technique with the amusing acronym of CARS, or coherent anti-Stokes Raman spectroscopy. One useful application of CARS is to study the proteins present in a biological sample without disturbing it: even in a living cell. Fluorescence microscopy is a widelyused technique for identifying proteins in a cell, but it entails marking the proteins of interest by attaching other, very large, light-emitting molecules to them, which may disturb their normal function and kill the cell. It is like filming a wildlife documentary by taping a television camera to the tiger's head, while CARS is the silent cameraman in the treetops.

In order to provide all the different amounts of energy for the CARS technique, we use light of different frequencies. Light carries energy in an amount inversely proportional to its wavelength. Our eyes perceive light's wavelength as color. Obtaining intense laser light of an arbitrary wavelength is more difficult than it sounds, as lasers commonly (but not always) emit light of one fixed wavelength. We use another nonlinear optical technique, optical parametric amplification, to generate that light in a device called an optical parametric oscillator (OPO), explained in detail in chapter 2. An OPO takes laser light of one wavelength, and splits it into two other wavelengths, which can be varied ("tuned") in certain proportions.

It is almost like a prism, but not quite. A prism takes white light and splits it into

its component rainbow of colors; but monochromatic, let us say green, laser light is not a mixture of anything except one specific shade of green. If directed through a prism, it will remain green. This green light wave carries a certain amount of energy, and an OPO splits it into two other colors whose energy adds up to that of the original green. The "tuner" determines which branch receives which proportion of the energy, and thus which wavelengths emerge from the OPO.

It is convenient, for several reasons, to split the green light into two wavelengths of infrared light. Infrared is invisible to our eyes. However, like red light, our skin is partially transparent to it, which makes it quite useful for medical imaging applications. One can easily demonstrate this by shining a white-light flashlight in one's mouth in a darkened room; one's face will light up red.

The following two chapters describe the theory that the author considers necessary to understand OPOs and CARS, respectively. They are followed in turn by two chapters on experiments performed by the author as part of the requirements for his Master's degree in applied physics at the University of Twente.

The goal of this research was to rebuild and characterize the OPO described in Bouwmans [4], and to demonstrate CARS spectroscopy at the lowest possible energy. The author performed CARS spectroscopy experiments on polystyrene, toluene, superglue, and ethanol, using a setup designed in conjunction with Garbacik [16].

The author has made an effort to avoid unnecessary abbreviations, but OPO and CARS are inevitable, and are used frequently throughout the text. The reader would do well to commit them to memory now before embarking on the rest of the manuscript.

2

Optical parametric oscillators

Narrowband coherent anti-Stokes Raman scattering (CARS) microscopy and spectroscopy require a laser light source of tunable wavelength. An optical parametric oscillator (OPO) is an often-used device, first demonstrated by Giordmaine and Miller in 1965 [18], that emits two variable-wavelength laser beams, by exploiting nonlinear optical effects. The following sections describe how an OPO works, starting with a brief tour of those parts of classical electrodynamics necessary to understand the underlying processes. The description of the OPO given here largely follows the approach of Ebrahimzadeh and Dunn [10, pp. 22.2–22.21].

2.1 Nonlinear optics

The propagation of light is governed by Maxwell's equations. In a medium without free charges, they read [19, p. 330]:

$$\nabla \cdot \mathbf{D} = 0, \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

$$\nabla \cdot \mathbf{B} = 0, \qquad \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}.$$
(2.1)

These equations contain all we need to know about the propagation of light. The interaction between light and matter, which is essential to nonlinear optics, is described in two additional relations: the first between the electric field **E** and the electric displacement **D**,

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P},\tag{2.2}$$

where **P** is the material's polarization; and the second between the magnetic field **B** and the auxiliary field **H**,

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}.$$
 (2.3)

We simplify (2.3) by assuming that the material's magnetization $\mathbf{M} = \mathbf{0}$ [41, p. 514]. From these we can derive the wave equation for the electric field in a dielectric medium without free charges:

$$\nabla^{2}\mathbf{E} = \frac{1}{c_{0}^{2}}\frac{\partial^{2}\mathbf{E}}{\partial t^{2}} + \mu_{0}\frac{\partial^{2}\mathbf{P}}{\partial t^{2}}.$$
(2.4)

In a linear medium, **P** is proportional to **E**, and we would introduce the permittivity ε of the medium as the constant of proportionality in order to derive the wave equation for the electric field in linear media,

$$\nabla^2 \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2},\tag{2.5}$$

where $c = 1/\sqrt{\epsilon\mu_0}$ is the phase velocity of light within the medium. However, at the heart of non-linear optics is the idea that **P** is not at all linearly proportional to **E**.

The physical meaning of the macroscopic polarization is that the medium's atoms behave like charged dipoles (i.e. nuclei and electrons). The incident wave's electric field causes the dipoles to oscillate at the wave's frequency. As the incident field gets stronger, the dipoles' response is no longer proportional to the field strength. The dipoles oscillate at other frequencies, and induce their own field, which means that some of the wave propagating through the medium is converted to other frequencies.

The polarization can be expanded as: [10, p. 22.2]

$$\mathbf{P} = \varepsilon_0 \left(\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \cdots \right), \qquad (2.6)$$

where the *n*th-order susceptibility $\chi^{(n)}$ is a tensor of rank *n*. Substituting (2.6) into (2.4) yields the wave equation for the electric field in a nonlinear medium:

$$\nabla^2 \mathbf{E} = \frac{1 + \chi^{(1)}}{c_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \sum_{n=2}^{\infty} \frac{\chi^{(n)}}{c_0^2} \frac{\partial^2 \mathbf{E}^n}{\partial t^2}.$$
(2.7)

The terms of second or higher order are often negligible (the magnitude of $\chi^{(2)}$ in nonlinear media is roughly eight orders of magnitude smaller than $\chi^{(1)}$, and the magnitude of $\chi^{(3)}$ is another eight orders smaller than that [10, p. 22.3]) in which case the linear approximation applies. However, since the invention of the laser, we have been able to generate electric fields of such magnitude that the second and higher order terms become significant, allowing us to observe interesting nonlinear effects.

2.2 Electromagnetic waves

Solutions to the wave equations (2.4), (2.5), and (2.7) can take many different forms. Propagating light is often described by a function of the form:

$$\mathbf{E}(\mathbf{r},t) = E(\mathbf{r},t)e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})},$$
(2.8)

where *E* is the complex amplitude of the wave's electric field, which is a function of space and time; $\omega = 2\pi c_0/\lambda_0$ is the angular frequency of the wave; and **k** is the wave vector, pointing in the direction of propagation and having magnitude $k = n\omega/c_0$.

The experiments in this research deal with pulsed laser light, with a Gaussian intensity cross-section, a Gaussian pulse shape, and a Gaussian spectral shape centered around a frequency ω . Such a wave can be written in cylindrical coordinates $\mathbf{r} = (s, \varphi, z)$ as:

$$\mathbf{E}(\mathbf{r},t) = E(z)e^{-s^2/\sigma^2}e^{-t^2/\tau^2}e^{i(\omega t - kz)} * \mathrm{III}(ft).$$
(2.9)

Here, * denotes the convolution operation, σ and τ are the 1/e radii of the spatial and temporal profiles, respectively, and III is the shah function (see appendix A.2), an infinite train of Dirac delta functions with which the expression for one pulse is convoluted so as to repeat it in time at frequency f. However, this expression is cumbersome, and in most cases, particularly the paraxial approximation $s \ll \sigma$, it can be approximated by a plane wave. Ebrahimzadeh and Dunn also postulate [10, p. 22.55] that the steady-state analysis of synchronously pumped OPOs with a continuous train of ultrashort pulses is identical to that of continuous-wave OPOs. Eq. (2.9) can thus be approximated by:

$$\mathbf{E}(\mathbf{r},t) = E(z)e^{i(\omega t - kz)}.$$
(2.10)

2.3 Three-wave mixing

The second-order nonlinear processes that underlie the optical parametric oscillator are optical parametric generation and optical parametric amplification. Let us consider an incident light wave consisting of two frequencies ω_1 and ω_2 ($\omega_1 > \omega_2$) with respective complex amplitudes E_1 and E_2 and wave vectors \mathbf{k}_1 and \mathbf{k}_2 :

$$\mathbf{E}(\mathbf{r},t) \propto E_1 e^{i(\omega_1 t - \mathbf{k}_1 \cdot \mathbf{r})} + E_2 e^{i(\omega_2 t - \mathbf{k}_2 \cdot \mathbf{r})} + \text{c.c.}$$
(2.11)



Figure 2.1. Energy diagrams of second-order nonlinear optical processes. (a) Second harmonic generation, where two photons of frequency ω_1 combine into one photon of double the original frequency; (b) sum frequency generation, where two photons of different frequencies combine into one photon; (c) difference frequency generation, where a photon of frequency ω_1 is influenced by a photon of frequency ω_2 to split into two photons. The solid horizontal line represents the ground state of the medium's molecules, and the dotted lines represent virtual states. (Based on Boyd [5, pp. 5, 8–9].)

All of the remarkable nonlinear effects occurring inside the medium are described by the polarization term of eq. (2.7) containing E^2 :

$$\begin{split} \mathbf{E}^{2} &\propto E_{1}^{2}e^{i(2\omega_{1}t-2\mathbf{k}_{1}\cdot\mathbf{r})} + \mathrm{c.c.} \\ &+ E_{2}^{2}e^{i(2\omega_{2}t-2\mathbf{k}_{2}\cdot\mathbf{r})} + \mathrm{c.c.} \\ &+ 2E_{1}E_{2}e^{i((\omega_{1}+\omega_{2})t-(\mathbf{k}_{1}+\mathbf{k}_{2})\cdot\mathbf{r})} + \mathrm{c.c.} \\ &+ 2E_{1}E_{2}^{*}e^{i((\omega_{1}-\omega_{2})t-(\mathbf{k}_{1}-\mathbf{k}_{2})\cdot\mathbf{r})} + \mathrm{c.c.} \\ &+ 2|E_{1}|^{2}+2|E_{2}|^{2}. \end{split}$$

Each pair of terms in (2.12) signifies a physical process: second harmonic generation of ω_1 , second harmonic generation of ω_2 , sum frequency generation, difference frequency generation, and optical rectification, respectively. These nonlinear processes are known as three-wave mixing.

All of these three-wave mixing processes involve two waves interacting to produce a third wave of a different frequency. The exception is optical rectification, which produces a constant polarisation component throughout the medium—although this can be considered a wave of zero frequency. The other three-wave mixing processes are illustrated in figure 2.1.

A parametric process is one where the initial and final quantum states of the system are identical [5, p. 13]. In this case, these three-wave mixing processes are parametric, because the medium's molecules start and end in the lowest energy state, or the

ground state. When they leave the ground state by absorbing an incident photon, they only do so briefly, as the uncertainty principle states that a virtual state can only exist for a time $\hbar/\Delta E$, where ΔE is the energy difference between the virtual state and the nearest real state [5, pp. 13–14].

2.4 Parametric generation and amplification

Optical parametric generation is the inverse process of sum frequency generation, in which a photon at frequency $\omega_1 + \omega_2$ breaks up into photons at frequencies ω_1 and ω_2 . This process, also known in the literature as parametric noise, parametric fluorescence, parametric downconversion, and parametric emission, can be understood as spontaneous emission of light caused by vacuum fluctuations [10, p. 22.8]. A detailed explanation is beyond the scope of this thesis; however, a short, self-contained treatise on the subject can be found in Gerry and Knight [17, pp. 312–313].

Optical parametric amplification is a special case of difference frequency generation, where energy is transferred from a strong field, called the *pump* field, at frequency ω_p , to a weaker field ω_s , and the remaining energy is dumped into a field ω_i ($\omega_s > \omega_i$). The fields at frequencies ω_s and ω_i are called the *signal* and *idler* fields for historical reasons. As in difference frequency generation, the frequencies must satisfy the following relation in order to conserve energy:

$$\omega_p = \omega_s + \omega_i. \tag{2.13}$$

From an incident field consisting of those three frequencies,

$$\mathbf{E}(\mathbf{r},t) \propto E_p e^{i(\omega_p t - \mathbf{k}_p \cdot \mathbf{r})} + E_s e^{i(\omega_s t - \mathbf{k}_s \cdot \mathbf{r})} + E_i e^{i(\omega_i t - \mathbf{k}_i \cdot \mathbf{r})} + \text{c.c.}$$
(2.14)

we will derive the coupled wave equations describing optical parametric amplification using a method similar to Svelto [41, pp. 514–7]. We refer interested readers to the details in appendix B. Although the coupled wave equations (B.15) are valid for any directions of propagation, one-dimensional versions will suffice for the present application, as the pump, signal, and idler beams are all collinear. This does not apply to birefringent phase matching (see section 2.6).

The one-dimensional coupled wave equations read:

$$\frac{dA_p}{dr} = -i\kappa A_s A_i e^{-i(\Delta k)r},$$

$$\frac{dA_s}{dr} = -i\kappa A_p A_i^* e^{i(\Delta k)r},$$

$$\frac{dA_i}{dr} = -i\kappa A_p A_s^* e^{i(\Delta k)r},$$
(2.15)

with the frequency-independent amplitude A, explained in eq. (B.14), defined as:

$$A_j = E_j \sqrt{\frac{n_j}{\omega_j}},\tag{2.16}$$

the phase mismatch Δk as:

$$\Delta k = k_p - k_s - k_i, \tag{2.17}$$

and the coupling parameter κ as:

$$\kappa = \frac{\chi_{\rm eff}}{c_0} \sqrt{\frac{\omega_p \omega_s \omega_i}{n_p n_s n_i}},\tag{2.18}$$

where χ_{eff} is the effective nonlinear coefficient, defined as the magnitude of the $\chi^{(2)}$ tensor along the relevant axis.

The Manley-Rowe relations are also derived in appendix B. In the one-dimensional case, they read:

$$\frac{d\phi_s}{dr} = \frac{d\phi_i}{dr} = -\frac{d\phi_p}{dr},\tag{2.19}$$

which can be interpreted to mean that for every pump photon destroyed, one signal and one idler photon are created. This is another expression of the conservation of energy (compare eq. (2.13)).

2.5 The optical parametric oscillator

At the heart of an optical parametric oscillator is a dielectric medium with nonzero $\chi^{(2)}$. This is only true for crystalline media without inversion symmetry, such as lithium niobate. In centrosymmetric crystals, $\chi^{(2)}$ and all other even-order susceptibilities are zero.

This nonlinear optical crystal is excited by a pump wave of frequency ω_p , causing a small fraction of the pump photons to break down into pairs of signal and idler photons by way of optical parametric generation. This fraction is far too small to achieve macroscopic conversion. The crystal is placed in a resonator cavity, similar to that of a laser, in which (in this case) only the signal wave resonates. The signal wave is fed back into the crystal to interact with the pump wave in an optical parametric amplification, converting a larger and larger fraction of the pump photons into signal and idler photons. Figure 2.2 shows a schematic view of an OPO.

The OPO in figure 2.2 is singly-resonant for the signal, meaning that only the signal wave resonates in the cavity and not the idler. It has a ring-cavity configuration, in which the resonant wave only passes through the crystal in one direction; another



Figure 2.2. Sketch of a singly-resonant, ring-cavity optical parametric oscillator. (Based on Bouwmans [4, p. 11].)

popular configuration is the V-cavity, in which the resonant wave traverses the crystal in both directions. Some configurations also output the signal using one cavity mirror, called an output coupler, that transmits a fraction of the signal beam; in this example, the signal is split using a variable output coupler in the cavity. Ebrahimzadeh and Dunn [10, pp. 22.14–15] describe several other possible OPO cavity configurations.

When the feedback loop in the cavity has become stable, the OPO is outputting three beams: a signal beam at frequency ω_s , an idler beam at frequency ω_i , and a leftover pump beam at frequency ω_p . We know from (2.13), a statement of the law of conservation of energy, that the signal and idler frequencies must add up to the pump frequency; but there are many combinations of frequencies that satisfy this requirement. The specific combination of frequencies is dictated by a different conservation law: that of momentum. Selecting the desired frequencies is achieved by phase matching.

2.6 Phase matching

Once the OPO is stably resonating, we can neglect the signal field's gain in amplitude, and we can also assume that the intensity of the idler wave grows from zero at the front face of the crystal to a certain value I_i at the end face. If we also assume that the pump field's intensity is greater than that of the signal field, then

we can also neglect the pump's loss of amplitude to parametric conversion [10, pp. 22.10–11].

Integrating the third equation of (2.15) over the length of the crystal L_c with constant A_p and A_s yields:

$$A_i(L_c) = -i\kappa A_p A_s^* L_c e^{\frac{1}{2}iL_c\Delta k} \operatorname{sinc} \frac{1}{2}L_c\Delta k, \qquad (2.20)$$

and by way of $I_j = \frac{1}{2}\omega_j \varepsilon_0 c_0 |A_j|^2$:

$$I_{i} = \frac{2\omega_{i}^{2}I_{p}I_{s}\chi_{\text{eff}}^{2}}{n_{p}n_{s}n_{i}\varepsilon_{0}c_{0}^{3}}L_{c}^{2}\operatorname{sinc}^{2}\frac{1}{2}L_{c}\Delta k.$$
(2.21)

Figure 2.3, a plot of the idler intensity against the normalized phase matching parameter $L_c\Delta k/2\pi$, shows that destructive interference severely limits the OPO output intensity, unless the phase mismatch is zero. Recalling (2.17), since the momentum of a photon is equal to $\hbar \mathbf{k}$, we can then state the law of conservation of momentum for optical parametric amplification, or *phase matching condition*,

$$\mathbf{k}_p = \mathbf{k}_s + \mathbf{k}_i, \tag{2.22}$$

or, if the beams are collinear in the crystal, $k_p = k_s + k_i$.

Only the signal and idler frequencies that satisfy the phase matching condition *and* the law of conservation of energy will be 'picked out' from the frequencies produced by parametric generation and amplified in the OPO.

In general, the phase matching condition is not met because of dispersion (variation in the index of refraction for different wavelengths). The three waves propagate at different phase velocities $c = n/c_0$, causing periodic repetition of constructive and destructive interference [10, p. 22.11]. The length of this period, that is, the length in which the waves' phase difference changes by π rad, is called the *coherence length* [10, p. 22.11]:

$$l_c = \pi / \Delta k. \tag{2.23}$$

The coherence length is the maximum crystal length that can be put to effective use for optical parametric amplification. Typical coherence lengths are in the order of tens of micrometers for parametric generation at visible and infrared wavelengths [10, p. 22.11], requiring an impracticably thin crystal.

However, the material's dispersion can be compensated: mineral crystals' indices of refraction often vary with the propagation direction within the crystal. In addition, crystals that exhibit two distinct indices of refraction for different polarization directions, such as calcite, are called *birefringent*. Since $k = n\omega/c_0$, the phase matching condition can be satisfied by varying the propagation angles and polarizations of



Figure 2.3. Theoretical dependence of the idler intensity on the normalized phase matching parameter $L_c\Delta k/2\pi$; it is apparent that almost no conversion takes place if the phase mismatch Δk is not zero. (Based on Ebrahimzadeh and Dunn [10, p. 22.11].)

the three waves so that they all propagate at the same phase velocity. This is called birefringent phase matching [10, p. 22.11] and is usually achieved by rotating the crystal. It can be fine-tuned by changing the crystal's temperature, which allows different combinations of signal and idler frequencies to be selected by changing the respective indices of refraction.

Birefringent phase matching has several drawbacks. It causes beam walk-off and it does not allow the waves to have the same polarization. Instead, a technique called quasi-phase matching is often employed [29]. Quasi-phase matching, first postulated by Armstrong *et al.* in 1962 [1], requires a *periodically poled* nonlinear crystal, in which the sign of the nonlinear susceptibility tensor (simplified in our model to the scalar χ_{eff}) is reversed once per coherence length, causing constructive interference throughout the whole crystal even though Δk is not zero everywhere. The phase matching condition then becomes:

$$k_p = k_s + k_i + \frac{2\pi}{\Lambda},\tag{2.24}$$

with the poling period $\Lambda = 2l_c$. The signal-idler frequency combination can be selected by changing the poling period. This is usually achieved by using a crystal with several different domains side-by-side. Sometimes a crystal with a 'fan-out'



Figure 2.4. Idler output intensity as a function of the crystal length normalized to the coherence length (L_c/l_c) , for different methods of phase matching. (Based on Boyd [5, p. 108].)

poling pattern is used, in which the poling period changes gradually. Once the poling period has been selected, the frequencies can be fine-tuned by changing the temperature of the crystal. The different types of phase matching are compared in figure 2.4.

An analytical expression for the quasi-phase-matched idler intensity in figure 2.4 is derived in appendix B.3. The other curves are obtained from eq. (2.21). It should be noted that an approximation of quasi-phase matching for $L_c \gg l_c$ can be obtained by multiplying (2.20) by $2/\pi$ or (2.21) by $4/\pi^2$ and treating Δk as if it were zero [30].

Quasi-phase matching thus produces $4/\pi^2$ times less intensity on average than birefringent phase matching. However, it is not tied to any particular direction or polarization, allowing free use of the axis and polarization with the highest nonlinear susceptibility. Since the idler intensity is proportional to the square of χ_{eff} (2.21), quasi-phase matching often turns out to be more efficient than birefringent phase matching.

2.7 Pump threshold

When the OPO is pumped with enough power so that the signal gain through the crystal exactly equals the signal loss in the cavity, it will start to oscillate. To calculate this pump threshold, using the method in Tukker [43, pp. 16–17], we must drop the assumption of constant A_s . The coupled wave equations (2.15) then transform to a pair of damped oscillation equations. Solving them for $r = L_c$ and $A_i(0) = 0$ yields the following:

$$A_{s}(L_{c}) = A_{s}(0)e^{i\Delta kL_{c}/2}\left(\cosh\Gamma L_{c} - \frac{i\Delta k}{2\Gamma}\sinh\Gamma L_{c}\right),$$

$$A_{i}(L_{c}) = -A_{s}^{*}(0)e^{i\Delta kL_{c}/2}\frac{i\kappa A_{p}^{*}}{\Gamma}\sinh\Gamma L_{c},$$
(2.25)

where Γ is the parametric gain coefficient:

$$\Gamma = \sqrt{\kappa^2 |A_p|^2 - (\Delta k)^2/4}.$$
(2.26)

When $\Delta k = 0$, as it is on average in quasi-phase matching, we can write:

$$A_s(L_c) = A_s(0)\cosh(\kappa |A_p|L_c).$$
(2.27)

A small fraction α_s of the signal is lost on each round trip through the cavity:

$$A_s(0) = (1 - \alpha_s) A_s(L_c).$$
(2.28)

For the cavity to resonate, the signal gain through the crystal must equal the signal loss in the cavity on each round trip. If we assume that $\kappa |A_p|L_c \ll 1$, we can combine (2.27) and (2.28) and write the hyperbolic cosine as a second-order Taylor expansion:

$$(1 - \alpha_s)(1 + \frac{1}{2}\kappa^2 |A_p|^2 L_c^2) = 1,$$
(2.29)

which eventually, by way of $P_p = n_p \omega_p c_0 |A_p|^2$, yields an expression for the threshold pumping power:

$$P_{\rm thr} = \frac{\alpha_s \varepsilon_0 n_p^2 n_s n_i \lambda_{s0} \lambda_{i0}}{8\pi^2 \chi_{\rm eff}^2 L_c^2}.$$
(2.30)

2.8 Conversion efficiency

The conversion efficiency η , defined as the ratio of the number of converted pump photons to the number of incoming pump photons, can be expressed as any of several equivalent definitions:

$$\eta = \frac{\phi_{(s,i)}}{\phi_p} = \frac{\lambda_{(s,i)0} P_{(s,i)}(L_c)}{\lambda_{p0} P_p(0)} = \frac{P_s(L_c) + P_i(L_c)}{P_p(0)} = 1 - \frac{P_p(L_c)}{P_p(0)}.$$
 (2.31)

A more useful expression is derived in Tukker [43, pp. 17–18]. We return once more to the coupled wave equations (2.15). Since the cavity is oscillating, we can assume constant A_s for the time being. However, the loss of pump power through the crystal is now important, so we drop the assumption of constant A_p . Once again eliminating one of the coupled wave equations, the other two transform to a pair of damped oscillation equations, of which the solution is, for $r = L_c$ and $A_i(0) = 0$:

$$A_{p}(L_{c}) = A_{p}(0)e^{-i\Delta kL_{c}/2}\left(\cos\beta L_{c} + \frac{i\Delta k}{2\beta}\sin\beta L_{c}\right),$$

$$A_{i}(L_{c}) = A_{p}(0)e^{i\Delta kL_{c}/2}\frac{i\kappa A_{s}^{*}}{\beta}\sin\beta L_{c},$$
(2.32)

where β is the parametric gain coefficient (compare eq. (2.26)):

$$\beta = \sqrt{\kappa^2 |A_s|^2 + (\Delta k)^2 / 4}.$$
(2.33)

The first of eqs. (2.32) can be multiplied by its complex conjugate and written as:

$$P_p(L_c) = P_p(0) \cos^2 \beta L_c,$$
 (2.34)

if we once again assume that $\Delta k = 0$ on average. In order to obtain an expression for β and thus the conversion efficiency, we must once again drop the assumption of constant A_s . Substituting eqs. (2.32) into the second of eqs. (2.15) and integrating yields:

$$A_s(L_c) = A_s(0) \left(1 + \frac{1}{2} \kappa^2 L_c^2 |A_p(0)|^2 \operatorname{sinc}^2 \beta L_c \right).$$
(2.35)

Writing (2.35) as a function of the normalized pump power $P_N = P_p(0)/P_{\text{thr}}$ and substituting (2.27) and (2.28) eventually yields:

$$P_N = \frac{1}{\operatorname{sinc}^2 \beta L_c}.$$
(2.36)

By the last definition of (2.31), the efficiency is then:

$$\eta = 1 - \cos^2 \arcsin \sqrt{\frac{1}{P_N}},\tag{2.37}$$

in which arcsinc represents the principal inverse of the sinc function, for which there is no simple analytical expression. However, it is trivial to show that the entire pump wave is converted (i.e., $\eta = 1$) if the OPO is pumped at $\pi^2/4$ times the threshold power. Past that point, signal and idler photons recombine to form pump photons, which is known as back-conversion.

In practice it is impossible to convert 100% of the pump wave. This discrepancy arises from the paraxial approximation of section 2.2 in which waves with Gaussian spatial and temporal (i.e., pulsed) profiles were simplified to continuous plane waves [43, p. 18].



Figure 2.5. Conversion efficiency η for continuous plane waves and pulsed Gaussian beams as a function of the normalized pump power $P_N = P_p(0)/P_{\text{thr}}$. When pumping with a pulsed Gaussian beam, the maximum conversion efficiency is about 63% and it is reached at $P_N \approx 6.5$. (Based on Tukker [43, p. 22].)

Bjorkholm [2] derives an expression for waves with a Gaussian spatial profile. The mathematics are beyond the scope of this thesis, but interested readers are referred to the aforementioned source. The conversion efficiency for an ideal Gaussian pump beam is approximated by:

$$\eta = 1 - \frac{1}{P_N} - \int_0^{\ln P_N} \cos^2\left(\operatorname{arcsinc}\sqrt{\frac{e^a}{P_N}}\right) e^{-a} \, da \tag{2.38}$$

Tukker [43, pp. 18–21] asserts that (2.38) holds for a Gaussian pump beam with a rectangular temporal pulse shape, but provides a method for carrying out numerical approximations for waves with the form of (2.9), shown in fig. 2.5.

3

Coherent anti-Stokes Raman scattering

When light passes through an inhomogeneous medium, interactions with molecules cause it to scatter. The phenomenon of inelastic scattering occurs when the scattered light has a different wavelength than the incident light, and it includes Raman scattering. This was predicted in 1923 by Smekal [36] and demonstrated five years later by Raman and Krishnan [31]. Raman scattering grants a look at the vibrational properties of molecules, and has therefore been used as a spectroscopic technique since.

The phenomenon that would later come to be called coherent anti-Stokes Raman scattering (CARS), was discovered by Maker and Terhune [28], appropriately at the Ford Motor Company. CARS has several advantages over Raman scattering as a spectroscopic or microscopic technique. These will be discussed in this chapter, after a brief summary of the underlying theory of Raman scattering and CARS.

3.1 Elastic and inelastic scattering

A photon encountering a molecule may interact with it and scatter, similar to the way two masses may undergo elastic collision. The molecule absorbs the photon and re-radiates it in a random direction. There is no change in the photon's energy, and therefore its wavelength remains the same. This is called elastic scattering, or Rayleigh scattering. Its efficiency depends on the fourth power of the photon's



Figure **3.1.** *Sketch of the relative separation of energy levels of (a) electronic excited states, (b) vibrational states, and (c) rotational states.*

energy, and this fact is responsible for the blue color of the sky: blue photons have more energy than red photons and therefore scatter more readily from air molecules.

However, just as masses may undergo inelastic collision, where some of the kinetic energy is dissipated, photons may also scatter inelastically. The molecule absorbs the photon and re-radiates a photon with less energy. This happens when some of the photon's energy is converted to orbital, vibrational, or rotational energy in the molecule.

When a molecule absorbs enough energy, an electron may be promoted to a higherenergy orbit; this is known as an electronic excited state. After a certain time, dependent on the nature of the excited state, the electron decays back to the lowestenergy orbit, or ground state. At lower energies, each electronic state is divided into vibrational states, each of which represents the energy of a mode of vibration of one or more of the molecule's atoms. Each vibrational state is split into still lower-energy rotational states, representing rotation of the molecule's atoms. These energy levels are illustrated in figure 3.1. Raman spectroscopy is usually concerned with the vibrational states.

3.2 Molecular vibrations

The number of vibrational modes possible in a molecule depends on the number of atoms N. Each atom has three degrees of freedom, representing movement in three dimensions. Three of the molecule's total degrees of freedom represent translation of the entire molecule in three dimensions, while three more represent rotation of

the entire molecule around three axes. If the molecule is linear (e.g., O_2) then there are only two possible rotations, not counting rotation around the axis of symmetry. The remaining degrees of freedom represent molecular vibrations. Therefore, there are 3N - 6 possible modes of vibration, or 3N - 5 in linear molecules [37, p. 8].

A vibrating molecular bond may be approximated by two masses connected by a spring, in which case Hooke's law gives the vibration frequency as a function of the bond strength and the masses of the atoms [37, p. 75–76]:

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} , \qquad (3.1)$$

where *k* is the spring constant of the bond between the atoms, and μ is the reduced mass of the atoms:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.\tag{3.2}$$

A molecular vibration of a certain frequency will be excited by an electromagnetic wave of the same frequency, as discussed in section 3.5.

3.3 Raman scattering

As stated before, a photon incident on a molecule may be absorbed and re-emitted. Raman scattering is when the re-emitted photon has a different energy than the absorbed photon. If the molecule is in the ground state at the start of the scattering process, then it may end up in a vibrational state and the scattered photon will have less energy. The ensuing shift in the light's frequency towards the red end of the spectrum is known as a Stokes shift, and the scattering process as Stokes Raman scattering. However, the molecule may already be in a vibrational state, due to thermal excitation. In that case it may end up in the ground state, and the scattered photon will have more energy, which is called anti-Stokes Raman scattering [37, p. 4–5]. The scattering processes are illustrated in figure 3.2.

The angular frequency of the vibrational mode, $\omega = 2\pi f$, is called the Raman shift Ω . From (3.1), we have:

$$\Omega = \sqrt{\frac{k}{\mu}} = |\omega_{\rm in} - \omega_{\rm Raman}|.$$
(3.3)

These processes can be characterized by their scattering cross-sections, a measure of the probability of scattering. Rayleigh scattering is the dominant process by far, with typical cross-sections on the order of 10^{-27} cm² [38]. Typical Raman cross-sections are 10^6-10^8 times smaller [37, p. 4]. Of these, far more are Stokes-shifted



Figure 3.2. Energy diagrams of scattering processes. (a) Rayleigh scattering, where a photon of frequency ω_i is re-emitted with no change; (b) Stokes Raman scattering, where a photon of frequency ω_i is re-emitted at a lower frequency ω_s , the energy difference being used to put the molecule into a vibrational state; and (c) anti-Stokes Raman scattering, where a photon of frequency ω_i incident on a molecule already in a vibrational state is reemitted at a higher frequency ω_{as} , the extra energy yielded by the molecule decaying from the vibrational state into the ground state. The dotted lines represent virtual states. The frequency difference between the ground state and the vibrational state, or the Raman shift, is denoted by Ω . (Based on Smith and Dent [37, p. 4].)

than anti-Stokes shifted, because relatively few molecules are in vibrational states to begin with. Indeed, Boltzmann's law states that the number of particles in an excited state [37, p. 73]:

$$\frac{N_e}{N_g} = \frac{g_e}{g_g} e^{-\frac{\hbar\Omega}{k_B T}},\tag{3.4}$$

where N_g and N_e are the number of molecules in the ground and excited vibrational states, respectively, g_g and g_e are the degeneracies of those states, k_B is Boltzmann's constant, and T is the temperature.

3.4 Vibrational spectroscopy

Raman spectroscopy entails illuminating a sample with monochromatic light, and recording the spectrum of the scattered light after filtering out the original illumination frequency. The Raman intensity is high at frequencies corresponding to vibrational energy levels, and therefore vibrational modes show up as peaks in the Raman spectrum. The set of vibrational modes is unique to every molecule, and therefore, a substance is identifiable given its Raman spectrum.

Figure 3.3 shows a typical Raman spectrum of a hydrocarbon molecule out of solution. In spectroscopy, it is usual to express energy differences as the wavenumber,



Figure 3.3. *Raman spectrum of polystyrene, typical for a bulk material. The peaks in the region around* 3000 cm^{-1} *are characteristic of* C–H *vibrations. The expanse between* $2000-2800 \text{ cm}^{-1}$ *, or the silent region, only houses bonds found less frequently in bio-organic molecules. The region from* 500 to 1500 cm^{-1} *is known as the fingerprint region. The data are from reference* [45].

often denoted by \tilde{v} . The wavenumber is generally expressed in inverse centimeters for historical reasons, and it is proportional to photon energy but independent of the speed of light:

$$\tilde{\nu} \equiv \frac{1}{\lambda_0} = \frac{E}{hc_0} = \frac{\omega}{2\pi c_0}.$$
(3.5)

Certain regions of Raman shifts can be said to correspond to certain types of chemical bonds. For example, the O–H bond of water and alcohols vibrates characteristically at $3100-3600 \text{ cm}^{-1}$. Various types of hydrogen-carbon bonds vibrate at $2800-3100 \text{ cm}^{-1}$, filling this region in any organic substance. The region from $2000-2800 \text{ cm}^{-1}$ is known as the silent region; only bonds infrequently found in bio-organic molecules vibrate there, such as triple bonds and carbon-deuterium bonds. Many double bonds, such as C=C and C=O, vibrate between 1400 and 1900 cm^{-1} . Last but not least, the region between 500 to 1500 cm⁻¹ is crowded with complex patterns of carbon-carbon and carbon-nitrogen vibrations unique to each molecule [37, p. 16]. It is therefore called the fingerprint region, as it can be used to identify molecules by "taking their fingerprints." A more comprehensive list of characteristic Raman vibrations can be found in Smith and Dent [37, pp. 15–19]. Not all molecular vibrations cause a Raman peak. Raman scattering arises from a change in the polarizability of the electron cloud around the vibrating bond. This is strongest in symmetric vibrations. Asymmetric vibrations, on the other hand, cause a change in the molecule's dipole moment, which produces a strong response in infrared absorption spectroscopy. In fact, in centrosymmetric molecules, a particular vibrational mode can be either Raman-active or infrared-active, but not both [37, pp. 6, 8].

3.5 Four-wave mixing

We will now leave Raman scattering for the moment and return to the nonlinear optics of the previous chapter. Just as the three-wave mixing processes in section 2.3 emerge from the second-order polarization term $\chi^{(2)} \mathbf{E}^2$ in (2.6), the third-order term $\chi^{(3)} \mathbf{E}^3$ gives rise to all sorts of four-wave mixing processes.

Four-wave mixing happens when three input waves combine to produce a fourth output wave; however, we are interested (for reasons which will become clear in the next section) in the case where two of the input waves are the same, or *degenerate* four-wave mixing. Let us once again consider an incident light wave consisting of two frequencies ω_1 and ω_2 , as in (2.11):

$$\mathbf{E}(\mathbf{r},t) \propto E_1 e^{i(\omega_1 t - \mathbf{k}_1 \cdot \mathbf{r})} + E_2 e^{i(\omega_2 t - \mathbf{k}_2 \cdot \mathbf{r})} + \text{c.c.}$$

Cubing this expression yields, similar to (2.12), a description of the degenerate four-wave mixing effects:

$$\mathbf{E}^{3} \propto 3E_{1}(|E_{1}|^{2}+2|E_{2}|^{2})e^{i(\omega_{1}t-\mathbf{k}_{1}\cdot\mathbf{r})} + \text{c.c.}$$

$$+ 3E_{2}(2|E_{1}|^{2}+|E_{2}|^{2})e^{i(\omega_{2}t-\mathbf{k}_{2}\cdot\mathbf{r})} + \text{c.c.}$$

$$+ E_{1}^{3}e^{i(3\omega_{1}t-3\mathbf{k}_{1}\cdot\mathbf{r})} + \text{c.c.}$$

$$+ E_{2}^{3}e^{i(3\omega_{2}t-3\mathbf{k}_{2}\cdot\mathbf{r})} + \text{c.c.}$$

$$+ 3E_{1}^{2}E_{2}e^{i((2\omega_{1}+\omega_{2})t-(2\mathbf{k}_{1}+\mathbf{k}_{2})\cdot\mathbf{r})} + \text{c.c.}$$

$$+ 3E_{1}E_{2}^{2}e^{i((\omega_{1}+2\omega_{2})t-(\mathbf{k}_{1}+2\mathbf{k}_{2})\cdot\mathbf{r})} + \text{c.c.}$$

$$+ 3E_{1}E_{2}^{2}e^{i((2\omega_{1}-\omega_{2})t-((\mathbf{k}_{1}-\mathbf{k}_{2})\cdot\mathbf{r}))} + \text{c.c.}$$

$$+ 3E_{1}^{2}E_{2}^{*}e^{i((2\omega_{2}-\omega_{1})t-(2\mathbf{k}_{2}-\mathbf{k}_{1})\cdot\mathbf{r})} + \text{c.c.}$$

$$+ 3E_{1}^{*}E_{2}^{*}e^{i((2\omega_{2}-\omega_{1})t-(2\mathbf{k}_{2}-\mathbf{k}_{1})\cdot\mathbf{r})} + \text{c.c.}$$

Each pair of terms in (3.6) once again signifies a physical process: generation of the input frequencies ω_1 and ω_2 , third-harmonic generation of ω_1 and ω_2 , sum frequency generation of ω_1 with the second harmonic of ω_2 and vice versa, and difference frequency generation of ω_1 with the second harmonic of ω_2 and vice versa. The latter two carry the whimsical acronyms of CARS and CSRS (pronounced 'scissors'), which stand for *coherent anti-Stokes Raman scattering* and *coherent Stokes Raman scattering*, respectively.



Figure 3.4. Energy diagram of CARS, where the interaction frequency $\omega_p - \omega_s$ is tuned to a molecular vibration Ω . The dotted lines represent virtual states. (Based on Smith and Dent [37, p. 192].)

3.6 Coherent anti-Stokes Raman scattering

Coherent anti-Stokes Raman scattering (CARS) is a parametric (see section 2.3) third-order nonlinear optical process. An energy diagram of CARS is shown in figure 3.4. Two waves, the *pump* wave at frequency ω_p and the *Stokes*¹ wave at frequency ω_s interact to drive a molecular vibration at frequency $\omega_p - \omega_s$, which interacts with the pump wave again to produce the *anti-Stokes* wave at frequency $\omega_{as} = 2\omega_p - \omega_s$. The second interaction with the pump wave is sometimes called the *probe* wave, especially if a third wave at frequency ω_{pr} is used instead of the pump.

Deriving an expression for the intensity of the CARS signal in a medium proceeds in much the same way as the first half of the derivation in appendix B, and thus will not be repeated here. It is a matter of taking an input wave,

$$\mathbf{E}(\mathbf{r},t) \propto E_p e^{i(\omega_p t - \mathbf{k}_p \cdot \mathbf{r})} + E_s e^{i(\omega_s t - \mathbf{k}_s \cdot \mathbf{r})} + E_{as} e^{i(\omega_{as} t - \mathbf{k}_{as} \cdot \mathbf{r})} + \text{c.c.},$$
(3.7)

where $E_{as}(\mathbf{0}) = 0$, and solving the wave equation, taking E_p and E_s to be constant. Starting from (B.9), we have:

$$\hat{\mathbf{k}}_{as} \cdot \nabla E_{as} = -\frac{3}{2} \frac{\omega_{as} \chi^{(3)}}{n_{as} c_0} E_p^2 E_s^* e^{i(\mathbf{k}_{as} - (2\mathbf{k}_p - \mathbf{k}_s)) \cdot \mathbf{r}}.$$
(3.8)

The expression $\Delta \mathbf{k} = \mathbf{k}_{as} - (2\mathbf{k}_p - \mathbf{k}_s)$ is the phase-matching condition for CARS, which will be discussed in section 3.7 (compare section 2.6.) Integrating (3.8) from r = 0 to the medium thickness *D* yields:

$$E_{as}(D) = -\frac{3}{2} \frac{\omega_{as} \chi^{(3)}}{n_{as} c_0} E_p^2 E_s^* \frac{1}{\Delta k} (e^{i\Delta kD} - 1).$$
(3.9)

¹The reader should note that the subscripts *p* and *s* do not mean the same as in chapter 2. The *s* now stands for Stokes, not signal, and the pump wave meant here is a different pump wave; indeed, in the experiments presented in chapter 5, the *signal* output of the OPO is used as the *pump* input for the CARS process.



Figure 3.5. The boxCARS crossed-beam phase matching scheme. By splitting the pump beam and having it enter the sample from an angle θ_p on either side, the anti-Stokes beam can be separated quite far from the other three, obviating the need for spectral filtering. (Based on Eckbreth [11].)

Using the same trick as in (2.20), and squaring to get the intensity, we obtain:

$$I_{as} = \frac{9\pi^2 \left|\chi^{(3)}\right|^2}{\varepsilon_0^2 c_0^4 n_p^2 n_s n_{as} \lambda_{as}^2} I_p^2 I_s D^2 \operatorname{sinc}^2 \Delta k D/2.$$
(3.10)

The detectable CARS signal is thus proportional to the Stokes intensity and the square of the pump intensity, so increasing the pump intensity has more of an effect than increasing the Stokes. The nonlinear susceptibility $\chi^{(3)}$ is proportional to the number of oscillators (and therefore vibrating molecules) in the interaction volume [14], and so the CARS signal is also proportional to the square of the concentration of the substance being examined. This is different than conventional Raman spectroscopy, where the Raman scattering is linearly dependent on the number of oscillators in the interaction volume [20].

3.7 Phase matching in CARS

In CARS, as in parametric amplification (compare eq. (2.22)), the output intensity has a squared-sinc function dependence on the phase mismatch Δk . However, using collinear beams causes a large phase mismatch, as many samples are dispersive (i.e., their index of refraction is wavelength-dependent.) When CARS microscopes were first constructed, they used non-collinear phase matching schemes. The most general of these is boxCARS [11], shown in figure 3.5.

In boxCARS, the pump beam is split and introduced into the sample on both sides from an angle θ_p . The Stokes beam is introduced from a larger angle θ_s and the phase matching condition ensures that the anti-Stokes beam leaves the sample from



Figure 3.6. Calculated Stokes and anti-Stokes angles for boxCARS phase matching as a function of the pump angle, taking dispersion into account. The values used for calculation are typical for probing the 3055 cm^{-1} Raman shift in toluene. The indices of refraction for the various wavelengths were calculated from Samoc [33].

a smaller angle θ_{as} . The latter angles can be calculated geometrically from the former, remembering that $|\mathbf{k}| = n\omega/c_0$:

$$\theta_{s} = \arccos \left\{ \frac{\left(\frac{2n_{p}}{\lambda_{p}}\cos\theta_{p}\right)^{2} + \left(\frac{n_{s}}{\lambda_{s}}\right)^{2} - \left(\frac{n_{as}}{\lambda_{as}}\right)^{2}}{4\frac{n_{p}n_{s}}{\lambda_{p}\lambda_{s}}\cos\theta_{p}}, \\ \theta_{as} = \arccos \left\{ \frac{\left(\frac{2n_{p}}{\lambda_{p}}\cos\theta_{p}\right)^{2} + \left(\frac{n_{as}}{\lambda_{as}}\right)^{2} - \left(\frac{n_{s}}{\lambda_{s}}\right)^{2}}{4\frac{n_{p}n_{as}}{\lambda_{p}\lambda_{as}}\cos\theta_{p}}. \right\}$$
(3.11)

The phase-matching Stokes and anti-Stokes angles are plotted in figure 3.6 as a function of the pump angle, for a typical dispersive medium.

BoxCARS is a generalized case of several other whimsically-named phase matching schemes, shown in figure 3.7. However, they all have the disadvantage of their Stokes and anti-Stokes angles depending on the wavelengths. This renders proper alignment highly impractical if working with variable wavelengths. In addition, they are unsuitable for microscopy, having a low resolution [14].

In 1999, Zumbusch et al. [46] used a microscope objective with a high numerical aperture to focus the beams into a tight cone. This introduces the pump and Stokes



Figure 3.7. Beam configurations for several CARS phase matching schemes. The addition of the wave vectors is shown in the insets. (a) Regular phase matching, a special case of boxCARS where $\theta_p = 0$. (b) BoxCARS [11], see figure 3.5. (c) Folded boxCARS [35], where the two pump wave vectors are in a different plane than the Stokes and anti-Stokes wave vectors. (d) Unstable-resonator spatially enhanced detection (USED) CARS [12], where the wave vectors are extended into a coaxial rings, so named because an unstable resonator was originally used to generate the ring mode. (Method of representation based on Jurna [22, p. 32] and Garbacik [16, p. 46].)

beams into the sample with an entire range of angles, allowing phase matching at any of the combinations of boxCARS angles present in the cone. The tight focus also keeps the interaction length short, which relaxes the phase matching condition, since less back-conversion can occur. This scheme is now universally used in CARS microscopy and imaging; however, it does require spectral filters to separate the anti-Stokes beam from the leftover pump and Stokes.

3.8 Resonant and nonresonant CARS

The reader will remember from (3.10) that the intensity of the CARS signal is quadratic in the nonlinear susceptibility $\chi^{(3)}$. This parameter increases dramatically when the pump and Stokes interaction at frequency $\omega_p - \omega_s$ is tuned to a molecular vibration Ω . We will denote the frequency difference between a vibrational resonance and the driving field by the *detuning* $\Delta = \Omega - (\omega_p - \omega_s)$.

If, however, the pump and Stokes interaction frequency is far from a vibrational resonance (i.e., the detuning is large), then there is still a CARS response at the anti-Stokes frequency ω_{as} . This is called *nonresonant* background, and does not occur in conventional Raman spectroscopy. A response at the anti-Stokes frequency can also be caused by an interaction frequency, for example $2\omega_p$, being near an electronic transition; this is called two-photon absorption. Energy diagrams of these processes are shown in figure 3.8 (compare figure 3.4).

The nonlinear susceptibility $\chi^{(3)}$ contains information about all of these contributions to the detected CARS signal at frequency ω_{as} . It can be modeled as the sum of complex Lorentzian functions [27]:

$$\chi^{(3)} \propto \chi^{(3)}_{NR} + \frac{A_{TP}}{\omega_{TP} - 2\omega_p - i\Gamma_{TP}} + \sum_R \frac{A_R}{\Omega_R - (\omega_p - \omega_s) - i\Gamma_R} , \qquad (3.12)$$

where A_j is the strength of the vibrational mode j, and Γ_j is its full bandwidth at half maximum. The two-photon term can be avoided by using near-infrared excitation wavelengths, which are not near enough to the electronic transition level to contribute to the CARS signal [46]. The intensity of spontaneous Raman scattering, on the other hand, is proportional to the imaginary part of the nonlinear susceptibility $\chi^{(3)}$ [20]:

$$I_{\text{Raman}}(\omega) \propto -\text{Im}\,\chi^{(3)}(\omega) = \sum_{R} \frac{A_R \Gamma_R}{(\Omega_R - \omega)^2 + \Gamma_R^2}.$$
(3.13)

Squaring the nonlinear susceptibility, in order to plug it into (3.10), yields a constant nonresonant term, a Lorentzian resonant term, and a mixing term [14]. Eq. (3.14)



Figure 3.8. Energy diagrams of nonresonant processes contributing a response at the CARS anti-Stokes frequency. (a) Nonresonant CARS. Note that there is no vibrational level where the driving frequency is tuned, and instead the combination of pump and Stokes frequencies puts the molecule into a virtual energy level, indicated by a dotted line. (b) Two-photon absorption. This process is enhanced by the virtual level at $2\omega_p$ being near the next electronic energy level, indicated by a thick line. Resonant CARS is shown in figure 3.4. (Based on Kamga and Sceats [24].)

illustrates this for the case of only one vibrational resonance:

$$\left|\chi^{(3)}\right|^2 \propto \left(\chi^{(3)}_{NR}\right)^2 + \frac{A^2}{\Delta^2 + \Gamma^2} + \frac{2A\Delta\chi^{(3)}_{NR}}{\Delta^2 + \Gamma^2}.$$
(3.14)

The terms from (3.14) are plotted separately in figure 3.9(a). Their sum, $|\chi^{(3)}|^2$, which is proportional to the CARS signal, is shown in figure 3.9(b), compared to the corresponding Raman signal. The CARS signal is slightly redshifted compared to the Raman signal, because of interference between the resonant and nonresonant CARS response. This interference is represented by the mixing term.

The interference therefore prevents the CARS spectrum from being interpreted quantitatively, especially in the fingerprint region with many lines close together [14]. In order to understand the interference, we must consider the phase of the CARS signal. It is no coincidence that a complex Lorentzian is used to model the molecular vibration: it is the model of a damped driven harmonic oscillator, where the oscillator represents the molecular vibration, with a natural resonance frequency of Ω , and the driving frequency is the interaction frequency of the light, $\omega_p - \omega_s$.


Figure 3.9. A molecular resonance modeled as a complex Lorentzian function. (a) The three components of $|\chi^{(3)}|^2$: resonant, non-resonant, and mixing. (b) The total CARS signal, which is the sum of the terms in (a), compared to the corresponding Raman signal. The CARS signal is slightly redshifted because of the mixing term, which represents the interference between the resonant and nonresonant CARS response.

The reader may easily verify, by swinging a pendulum made of a length of string and a weight, or by waving a flexible curtain rod, that the response of a driven oscillator, with natural resonance frequency ω_r , has three oscillation modes depending on the driving frequency ω :

- ($\omega \ll \omega_r$) The response is weak and in phase with the driving force.
- ($\omega \approx \omega_r$) The response is strong, and 90° out of phase with the driving force.
- $(\omega \gg \omega_r)$ The response is weak and in antiphase with the driving force.

Applying the above to CARS, the phase of the resonant contribution to the anti-Stokes wave must then undergo a flip as the detuning goes from one side of the resonance to the other. However, since the actual oscillating is carried out by negatively-charged electrons, the phase response is directly opposite to that of a pendulum. The phase of the nonresonant contribution is always zero, meaning that



Figure 3.10. Simulated Raman and CARS spectra of ethanol (left axis) and the phase of the CARS signal (right axis). Far away from the resonances, the phase is zero, since the CARS signal is mostly nonresonant; and near the resonances, it drops almost to $-\pi$ *.*

the total phase goes from zero to $-\pi$ and back again as the detuning moves across the resonance.

Figure 3.10 shows the Raman spectrum, CARS spectrum, and CARS phase response simulated for a molecule modeled² after ethanol (C₂H₅OH). The phase is actually the phase difference between the pump/Stokes waves and the anti-Stokes wave. It dips near the resonances, almost reaching $-\pi$ at the strongest resonance, since the resonant contribution dominates there; and returns to zero, i.e. the phase of the nonresonant contribution, far away from the resonances.

Measuring the phase of the anti-Stokes signal as well as the intensity allows the resonant term of (3.14) to be calculated and nonresonant and mixing terms to be discarded. This can be achieved by heterodyne detection, for example [23], but there is also a mathematical method for extracting the resonant term from the intensity without measuring the phase [44]. This allows CARS spectra to be compared directly to the well-known and well-catalogued Raman resonances.

²Ethanol's O–H vibration around 3300 cm⁻¹ is not included. It is not as prominent in CARS spectra due to dephasing, which the complex Lorentzian approach does not model.

4

Experimental setup

The setup used in these experiments is complex, and will therefore be broken down into several stages, shown schematically in figure 4.1, each discussed separately. Figures 4.3–4.8 show the optics and other components used in these stages. The components are indicated by codes, and the precise specifications of each component are listed by code in table C.5.

A green-pumped, picosecond-pulsed, temperature-tunable optical parametric oscillator generates the variable wavelengths necessary for scanning CARS spectroscopy. The OPO's signal is used as the pump-probe wavelength in CARS, and either the idler or the laser's fundamental infrared wavelength are used as the Stokes wavelength (see section 3.6) in two distinct modes of operation. The latter beam is delayed so that its pulses coincide with those of the pump-probe beam.

The Stokes beam is also modulated so that the anti-Stokes signal from the CARS process can be separated more easily from the background noise, which is often 1/f [4, p. 29], i.e. the noise contains fewer high-frequency components than low-frequency ones. By modulating the useful signal at a high frequency at which there is less noise, the low-frequency background noise can be discarded.

The reason why the Stokes beam is modulated and not the pump-probe beam is because the photomultiplier tube's sensitivity decreases exponentially at wavelengths longer than about 850 nm. The Stokes wavelength is 1064 nm or more, so any modulated Stokes light leaking through the filters is far less likely to produce a spurious signal.



Figure 4.1. Schematic of the various parts of the setup, including the detectors and controllers connected to a computer.

4.1 Design of the OPO cavity

The optical parametric oscillator described in Bouwmans [4, pp. 30–32] was rebuilt. Its cavity design was nearly identical, except that more accurate data were available on the index of refraction of the lithium niobate crystal [26]. Therefore the calculations are repeated here briefly.

The OPO cavity must have a certain optical path length, since consecutive signal pulses must overlap in order to achieve high conversion efficiency. The length of the crystal is also known, so we can write:

$$d_{\rm long} + 2d_{\rm short} + n_c L_c = \frac{c_0}{f_{\rm pulse}},\tag{4.1}$$

where d_{long} is the long distance between the two curved mirrors, and d_{short} is the distance between a curved mirror and the nearest end face of the crystal, illustrated in figure 4.2. The pulse frequency of the laser is f_{pulse} . The index of refraction n_c can be calculated using (C.1). It is dependent on the signal wavelength, which obviously varies, but we will assume a signal wavelength of 950 nm and a temperature of 100 °C for the purpose of designing the cavity. The distance only varies by a few tenths of millimeters over the entire temperature and wavelength range.

The cavity is easily analyzed using Gaussian beam optics. For a complete description of this formalism, see Saleh and Teich [32, pp. 26–36, 81–100]. Taking the center



Figure 4.2. Design parameters of the OPO cavity, without the variable output coupler. The beam widths and optical elements are not to scale. See eq. (4.1).

of the crystal as the plane of reference, the cavity roundtrip matrix is

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & \frac{1}{2}L_c/n_c \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & d_{\text{short}} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -2/R_m & 1 \end{bmatrix} \cdots$$
(4.2)
$$\begin{bmatrix} 1 & d_{\text{long}} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -2/R_m & 1 \end{bmatrix} \begin{bmatrix} 1 & d_{\text{short}} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & \frac{1}{2}L_c/n_c \\ 0 & 1 \end{bmatrix}$$

where R_m is the radius of curvature of the curved cavity mirrors. Writing d_{long} in terms of d_{short} and applying the stability criterion

$$\left|\frac{A+D}{2}\right| \le 1\tag{4.3}$$

allows us to calculate $d_{\text{short}} = 129.4 \text{ mm}$, which can vary approximately half a centimeter in either direction while remaining stable. The long distance is then $d_{\text{long}} = 3444.4 \text{ mm}$. The roundtrip matrix also allows us to calculate the signal beam's $1/e^2$ intensity radius at its waist within the crystal, $w_{0,s} = 39.66 \text{ µm}$, and the Rayleigh range $z_0 = 11.48 \text{ mm}$. This Rayleigh range seems to extend outside the crystal, but since it is an optical path length, it only occupies 5.20 mm of the crystal.

The necessary parameters for the pump beam focusing system were calculated using a slight modification of the simulation in Jurna [21, pp. 41–58]. Assuming a



Figure 4.3. Optics for preparing the Vanguard laser beam for pumping the OPO.

focusing lens $f_{\text{focus}} = 125 \text{ mm}$ as in Bouwmans [4], and overlapping the Rayleigh range of the pump and signal beams, we obtain $d_{\text{focus}} = 16.70 \text{ mm}$. The pump beam radius on the focusing lens is then $w_{\text{lens}} = 906.1 \text{ µm}$, and the radius at the beam waist is $w_{0,p} = 29.68 \text{ µm}$. All these parameters are also illustrated in figure 4.2.

When installing the variable output coupler (see section 4.3), the cavity length must be shortened by $(n_{\text{PBC}} - 1)l_{\text{PBC}} \approx 6.6 \text{ mm}$, where l_{PBC} is the length of the polarizing beam cube (13 mm) and n_{PBC} its index of refraction (BK7 glass, about 1.51 [34]). A similar consideration must be made when installing the birefringent filter (see section 4.3).

4.2 Laser setup

The first stage is used to prepare the laser output beam for pumping the OPO. Two different pump lasers were used at different times, so two versions of this stage are shown in figures 4.3 and 4.4. The pump lasers are described in section C.4 of the appendix. The pump laser used while building and testing the OPO was a Spectra Physics Vanguard frequency-doubled Nd:YVO₄ laser (LASER1, figure 4.3), which was later replaced by a modified Coherent Paladin frequency-doubled Nd:YVO₄ laser (LASER2, figure 4.4) with higher output power. The Paladin was modified to produce second-harmonic light instead of the usual third harmonic at 355 nm, and it was fitted with an extra output port for the fundamental 1064 nm wavelength. The Paladin's preparation stage was modified from Garbacik [16, pp. 26–27].

The Vanguard's output beam first passes through an optical isolator (OII), a oneway optical element that prevents back-reflected beams from re-entering the laser cavity and causing instabilities. This step is unnecessary for this experiment, but required for other experiments using the same laser. Next, the beam power of 2 W is attenuated by means of a variable beam splitter consisting of a half wave plate (HWP1) and a Glan-Taylor prism (GTP1). The leftover power is used for other experiments. The beam then passes through two irises (I1 and I2): one to block



Figure 4.4. Optics for preparing the Paladin laser beams for the OPO and CARS portions of the setup.

forward reflections from the optical isolator, and the other to block back reflections from optical elements further on.

The Paladin's second-harmonic output beam's power is much greater, about 12.5 W, and two variable beam splitters (HWP1/GTP1 and HWP2/GTP2) are required to attenuate it. The unused portion of GTP1's light was used for another experiment, and it was useful to be able to adjust the power entering this setup without disturbing the other one; and GTP1's internal reflections totaled more than 1 W, so a second beam splitter was deemed useful [16, pp. 26–27]. The beam is then positioned in a fashion similar to the Vanguard setup, but the configuration requires some extra mirrors and only one iris.

The beam, which was measured to have a $1/e^2$ intensity radius of 0.36 ± 0.01 mm at this point using the Vanguard, then passes through a Galilean beam expander (L1 and L2), consisting of a concave and convex lens with overlapped foci, working like a telescope. In practice, the laser beam is not perfectly collimated, so the focus of L1 lies 1.6 mm behind that of L2. The beam's radius after the expander was measured to be 0.87 ± 0.01 mm using the Vanguard.

After the beam expander, a half wave plate (HWP3) changes the polarization of the beam to match the $e \rightarrow e + e$ (Type IV) interaction in the crystal. This is not necessary in the Paladin setup since the second variable beam splitter (GTP2) already gives the beam the correct polarization. The beam is then sent through another iris (I3) to block back reflections from the next stage.



Figure 4.5. Optics composing the OPO cavity, variable output coupler, and various detection devices.

Unlike the second-harmonic beam, the fundamental wavelength of 1064 nm must be optically isolated (OI2). Then, another variable beam splitter (HWP3 and PBC1) attenuates the beam and sends the remainder to another experiment. The beam then passes through a Keplerian beam expander (L3 and L4), consisting of two convex lenses, normally with overlapping foci. The beam does not need expansion here, and so the beam expander only serves to collimate it. This requires the foci to be separated by 63 mm, giving a total distance between the lenses of 263 mm.

Finally, the beam enters a retroreflector (RR1) mounted on a translation stage, which allows control of the beam path length so that the pulses will arrive at the CARS setup at the same time as the pulses coming from the OPO.

4.3 OPO setup

The next stage, shown in figure 4.5, consists of the OPO cavity and the optics used to focus the laser beam properly. The lens used to focus the beam into the crystal (L5) was calculated to be placed 16.7 mm from M11, but since the actual beam radius w_{lens} is slightly smaller, the actual distance is about 23 mm. This distance even varies during tuning, since the pump beam's focus must coincide with the signal focus, which changes as the cavity gets slightly larger or smaller. No more than about 330 mW of power can be allowed at this point, or the crystal's anti-reflection coating may be damaged.

The crystal (NLC) is described in section C.2. The four cavity mirrors (M11, M12, M13, and M14) have a custom coating that is described in section C.1. They are designed to reflect most of the signal beam and transmit most of the pump and idler beams. Therefore, the idler and the leftover pump leave the cavity at M12. The flat mirror M14 is mounted on a translation stage in order to adjust the length of the cavity as the signal wavelength changes.

The half-wave plate HWP4 and polarizing beam cube PBC2 form the variable output coupler [4, p. 36]. The half-wave plate rotates the *e*-polarized light by a certain amount and the beam cube removes the newly-rotated *o*-polarized component, sending it on to the next stage and leaving only *e*-polarized light to resonate in the cavity, thus effectively allowing any desired amount of signal light to be coupled out of the cavity.

The cavity also contains a birefringent filter (BRF), or Lyot filter. This filter's spectral transmission function is a comb of narrow peaks, the positions of which can be controlled by rotating the filter. It is useful for fine-tuning the signal and idler wavelengths, but it is usually left at its non-selective setting. Its current orientation requires o-polarization, and therefore HWP5 and HWP6 are necessary to rotate the e-polarization to o and back again.

A small fraction of the signal is transmitted by the cavity mirrors. This fact is exploited by placing various detectors in the light leaked from M14. The light is split using a glass plate (GP), and picked up by a CCD camera (CCD) and a wavelength meter (WLM). Neither of these devices is sensitive to the idler wavelengths, but the pump light must be removed using longpass filters (F3 and F5). The camera light is also attenuated using a neutral density filter (F4) and focused on the sensor using a lens (L7). The camera provides an image of the signal's spatial mode inside the cavity, which must be TEM₀₀ for the best CARS results.

Some light is also leaked from the output coupler due to internal reflections. This light is sent to a spectrum analyzer (sA) by means of a fiber coupler (FC) into which the light is gathered by an infrared-coated lens (L6). Another iris (15) serves to adjust the amount of light entering the fiber, as the spectrum analyzer can easily become saturated. A neutral density filter (F1) attenuates the light and a longpass filter (F2) removes the leftover pump light.

4.4 Signal and idler preparation

After being coupled out of the cavity, the signal beam enters another stage (figure 4.6) to prepare it for the CARS experiment. A longpass absorption filter (F6) removes the leftover pump light and a half-wave plate (HWP7) rotates the beam polarization to the appropriate direction for CARS. A small amount of light is leaked



Figure 4.6. Optics preparing the signal beam for the CARS experiment.

in a reflection from F6's surface, which again passes a longpass filter and neutral density filter (F7 and F8) and is detected by a silicon photodiode (PD1). This photodiode measures a value proportional to the signal power produced by the OPO. Its signal is digitized after being processed by a home-built decade amplifier.

Meanwhile, the idler beam enters another similar stage (figure 4.7). The beam is expanded using a Keplerian beam expander (L8 and L9) in order to fill the microscope objectives in the CARS setup (see section 3.7 and figure 4.8). As before, the lenses' foci do not coincide exactly, but are separated by 28 mm in order to collimate the beam.

A longpass absorption filter (F9) filters the unconverted fraction of the pump light out of the idler beam; this is where most of the unused pump light ends up. A retroreflector (RR2) is used to delay the beam so that the idler pulses arrive at the CARS setup at the same time as the signal pulses. This retroreflector leaks a small amount of light, which is a convenient point to measure the idler power with an indium gallium arsenide (InGaAs) photodiode (PD2) in the same way as the signal. This signal is amplified using another home-built decade amplifier, and then digitized. An iris (I5) is used to minimize the amount of ambient light incident on the photodiode.

4.5 CARS setup

The CARS setup (figure 4.8) was modified from Garbacik [16, pp. 46–49]. It can be operated in two modes: either the idler beam from the OPO can be used as the Stokes wavelength for CARS (hereafter 'idler mode'), or the fundamental 1064 nm wavelength from the laser ('1064 nm mode'). In each case, the Stokes beam is modulated using an optical chopper (CH) at 490 Hz and the unused beam is blocked.



Figure 4.7. Optics for preparing the idler beam for the CARS experiment and removing the unconverted pump light from the idler beam.



Figure 4.8. Optics composing the CARS experiment.

The beams must overlap spatially and their pulses must coincide temporally for CARS to occur. Temporal overlap is achieved by delaying the beams using retrore-flectors (RR1 and RR2). Dichroic mirrors (M26 and M28) are used to achieve spatial overlap. The dichroic mirror is transparent to one of the wavelengths, and reflects the other one, which is positioned using the dichroic and another mirror (M25 and M27 respectively).

The spatial and temporal overlap can both be verified by placing a nonlinear crystal (potassium titanium oxide phosphate, or KTP), cut for infrared second-harmonic generation, in OL1's focus. The second harmonics of the pump-probe and Stokes beams are then visible to the eye. If the beams are spatially and temporally overlapped, they are joined by a third color, the sum frequency of the two (see section 2.3).

The combination of the pump-probe and Stokes beam is focused on the sample us-

Filter	Transmitted	Observable	Component	
set	wavelengths (nm)	Idler mode	1064 nm <i>mode</i>	filters
1	580–750	2624–3677		F12, F13, F14
2	750-850	1578–2624	1184–1838	F15, F16, F17
3	750–900	1142–2624	857–1713	F15, F16

Table 4.1. Filter sets used to observe the anti-Stokes beam from the CARS process. See table C.5 for the specifications of the component filters.

ing an NA = 0.60 microscope objective lens (OL1) and collected using an NA = 0.40 collection objective (OL2). The filter FS represents a set of filters that must be changed according to the wavelengths used in the CARS process. The filters composing FS are shown in table 4.1. The other two filters (F10 and F11) are shortpass filters which remove any leftover Stokes light from the anti-Stokes beam, since the Stokes light is modulated and may cause a spurious signal.

The anti-Stokes signal is detected by a photomultiplier tube (PMT). Its output is amplified by a home-built decade amplifier, digitized, and processed by a software lock-in amplifier written in LabVIEW, extracting signals modulated at the chopper frequency.

5

Results and discussion

The present work consists of two parts: characterizing an optical parametric oscillator (OPO), and performing coherent anti-Stokes Raman scattering (CARS) measurements. Sections 5.1 through 5.4 discuss measurements characterizing the OPO and sections 5.5 through 5.7 discuss the results obtained from the CARS experiments. Note that the former were performed using the Vanguard pump laser and the latter using the Paladin (see section 4.2) except where otherwise noted.

5.1 OPO temperature tuning and scanning

The OPO emits tunable infrared light of 880–1040 nm (signal) and 1090–1350 nm (idler). The wavelength is limited on both sides by the reflection coating on the cavity mirrors (section C.1), which permit operation almost to the degeneracy point (at which the signal and idler wavelengths are the same, 1064 nm.)

The OPO's temperature tuning curve is shown in figure 5.1, measured using an automated data acquisition routine in LabVIEW. The solid lines are calculated according to (C.1) through (C.4). The measured data do not follow the calculated lines exactly, because the wavelength combination is not only dependent on the temperature and poling period, but also varies slightly if the cavity is realigned [4, p. 34] (see also section 5.4). In addition, the wavelength exhibits a slight hysteresis when changing the temperature [16, p. 58], as evidenced by the measurements around T = 115 °C on the $\Lambda = 6.85$ µm and $\Lambda = 6.90$ µm curves.



Figure **5.1***. Temperature tuning curve of the OPO. The signal wavelength was measured while changing the temperature, and the idler wavelength was calculated from the signal wavelength.*

Figure 5.2 shows the maximum idler output power plotted against the crystal temperature. This curve's oscillating form is characteristic of a dielectric coating and can probably be explained by the cavity mirrors' custom coating. The cavity losses and therefore the pump threshold are proportional to the fourth power of the reflectivity of this coating.

The OPO's output wavelengths can be tuned semi-continuously by changing the crystal temperature gradually. This can be done to a certain extent without realigning the cavity. Depending on how well the cavity is aligned, and how close the wavelength is to the degeneracy point, continuous scanning can be achieved for 12–18 nm to either side of the signal wavelength at alignment. After that, the cavity length must be adjusted to compensate, because the changing wavelength gives the crystal a different optical path length, and this changes the total length of the cavity; see eq. (4.1).

While scanning, the wavelength does not vary continuously, but executes a series of discrete jumps. This mode-hopping behavior is similar to that described by Ebrahimzadeh and Dunn [10, p. 22.21–22.28] but does not concern hopping from one single mode to another; since the pump light is pulsed, many modes are oscillating in the cavity at any given time. The cause is probably local maxima and minima in the gain bandwidth, with oscillation switching from one local maximum



Figure 5.2. Maximum idler output power as a function of the crystal temperature. The solid line is a guide to the eye.

to another as the phase-matching bandwidth is moved by changing the temperature.

Detuning (i.e. changing) the cavity length broadens the spectrum of the output pulses and eventually causes double or triple-peaked pulses. While exhibiting this multi-mode behavior, the OPO produced about twice the output power of single mode. If one is not concerned with the pulse shape, then the possible scan range is therefore far longer. However, the broader pulses proved unsuitable for CARS, and this was therefore not investigated.

5.2 OPO conversion efficiency and output power

In order to get an accurate measure of the OPO's power threshold, the conversion efficiency was calculated by measuring the idler output power at different pumping levels, with the variable output coupler set to minimize the signal output. The pump threshold for the lowest possible cavity losses was calculated by fitting the measured data to (2.38), assuming that the highest measured pump power was not enough to reach peak efficiency.

Figure 5.3 shows the measured data and the theoretical curve according to Tukker [43], and figure 5.4 shows the idler output power as a function of the pump input



Figure 5.3. Conversion efficiency of the OPO, simulated and measured.

power, along with the theoretical curve calculated from (2.31).

The value $P_{\text{thr}} = 29.4 \pm 0.9 \text{ mW}$ calculated from the conversion efficiency data agrees well with the value calculated from (2.30), $P_{\text{thr}} = 32.9 \pm 0.3 \text{ mW}$. This value assumes that $\alpha_s = 1 - R_s^4$, where R_s is the reflectivity of the cavity mirrors for the appropriate signal wavelength (see appendix C.1). Pumping the OPO slightly lower than the threshold can sometimes produce a small amount of output, but it seems to be the result of parametric generation from the crystal, which is not enough to resonate.

5.3 Variable output coupler

Unlike most singly resonant OPOs, in which one of the cavity mirrors is partially transparent (< 10%) for the resonating wavelength range, this one uses a variable output coupler. As explained in section 4.3, the coupler rotates the *e*-polarised light through an angle θ_{oc} and removes the *o*-polarized component from the cavity. We can write:

$$T_{oc} = \cos^2 \theta_{oc}, \tag{5.1}$$



Figure 5.4. Maximum OPO idler output power, simulated and measured. These data were recorded under conditions of minimum cavity loss, i.e. with the variable output coupler set to minimize the signal output.

and thus from (2.30):

$$P_{\rm thr} = \frac{R_s^4 \varepsilon_0 n_p^2 n_s n_i \lambda_{s0} \lambda_{i0}}{8\pi^2 \chi_{\rm eff}^2 L_c^2} \cos^2 \theta_{oc} = C \cos^2 \theta_{oc}.$$
 (5.2)

We can derive an expression for the total output power as a function of θ_{oc} . Eq. (2.31) shows that the total output power $P_s + P_i = \eta P_p$. Writing (2.38) with the pump threshold as in (5.2) while keeping the input pump power constant, we obtain:

$$P_s + P_i = P_p - C\cos^2\theta_{oc} - P_p \int_{0}^{\ln\frac{P_p}{C\cos^2\theta_{oc}}} \cos^2\left(\operatorname{arcsinc}\sqrt{\frac{C\cos^2\theta_{oc}}{P_p}}e^a\right) e^{-a} \, da. \quad (5.3)$$

Although this model is based on continuous-wave pumping, we can use it to explain the form of the measured results qualitatively and approximately. Figure 5.5 shows the signal, idler, and total output power as a function of the output coupler's polarization angle. These measurements suggest that the output coupler has a loss term that grows as the angle deviates from the angle of least output coupling. We take this loss term to be quadratic and fit appropriate parameters. If we then assume that the total signal power at the end face of the crystal is proportional



Figure 5.5. Signal and idler output power, and total power, as a function of the variable output coupler polarization angle. The solid lines are qualitative predictions from a model based on continuous-wave Gaussian pump beams. This model qualitatively explains the shape of the total output power curve and the 'shoulders' visible in the idler power measurements.

to $\cos^2 \theta_{oc}$, and that the output coupler removes a fraction thereof proportional to $\sin^2 \theta_{oc}$, then we can also approximate the shapes of the individual signal and idler powers.

The angle at which maximum signal output occurs seems to vary according to the pump power, shown in figure 5.6; the idler is always at its maximum at 90°, since no signal power is coupled out of the cavity at that angle.

5.4 Spectral characteristics

The signal spectrum can be measured with a spectrometer. The spectrum has an approximate Gaussian form. Figure 5.7 shows a typical signal spectrum measurement using the Vanguard, along with a Gaussian fit. The spectrometer is known to broaden the spectrum by 0.5 nm [4, p. 32]; this is taken into account in the fit.

The spectral width during a temperature scan with the Vanguard is shown in figure 5.8. The optimum scanning range is indicated in the figure. As discussed in



Figure 5.6. Output coupler polarization angle for maximum output coupling at different pump powers.



Figure 5.7. Typical signal spectrum of the OPO when pumped by the Vanguard. The Gaussian fit is corrected for the spectrometer's systematic broadening of 0.5 nm [4, p. 32].



Figure 5.8. Spectral full width at half maximum, during a temperature sweep from T = 72.0-140.0 °C pumped by the Vanguard. Spectral measurements to which a Gaussian could not be fitted with a correlation coefficient R > 0.95 are omitted. The arrows indicate the approximate temperature scan range producing the narrowest pulses. The solid line is an approximate indication of the average spectral width in this range.

section 5.1, the spectrum becomes broader outside of this range and eventually becomes multi-peaked. Selected signal spectra from the very edge of a temperature scan, illustrating these phenomena, are shown in figure 5.9.

The OPO's output spectrum when pumped by the Paladin is broader by an order of magnitude; however, CARS requires fairly narrow pulses. This means that the optimum scanning range of figure 5.8 becomes the only possible scanning range when using the Paladin. Figure 5.10 shows measurements acquired during a spectroscopic scan using an automated data acquisition routine in LabVIEW. The average full spectral width at half maximum $\Delta \tilde{\nu}$ is 26.0 ± 1.3 cm⁻¹ (standard deviation), if the OPO is aligned properly. This figure can be used to calculate the CARS spectral resolution, which Cheng et al. [6] estimate to be:

$$\Delta \tilde{\nu}_{\text{CARS}} = \sqrt{\Delta \tilde{\nu}_{\text{pump}}^2 + \Delta \tilde{\nu}_{\text{Stokes}}^2} .$$
 (5.4)

The full spectral width at half maximum $\Delta \tilde{v}_{1064}$ of the 1064 nm beam can be calculated using the time-bandwidth product of a Gaussian pulse [41, p. 335]:

$$\Delta t \Delta f = 2 \ln 2 / \pi \approx 0.441. \tag{5.5}$$



Figure 5.9. Evolution of the signal spectrum near the end of a temperature sweep, illustrating broadening and multiple modes.



Figure 5.10. Spectral full width at half maximum, during a series of six CARS scans pumped by the Paladin. The region beyond 960 nm illustrates the broadening effect that happens when leaving the optimum scanning range.



Figure 5.11. Comparison of the 1585 and 1603 cm⁻¹ lines in polystyrene, in idler mode (calculated spectral resolution $\Delta \tilde{v} = 36.8 \text{ cm}^{-1}$) and 1064 nm mode ($\Delta \tilde{v} = 26.0 \text{ cm}^{-1}$). In the latter mode, the two neighboring peaks are easily resolvable. Compare to figure 3 of Cheng [7].

The pulse length of 15 ps given in table C.4 yields a spectral width of $\Delta \tilde{\nu}_{CARS} = 1.0 \text{ cm}^{-1}$. Therefore, the CARS spectral resolution is $36.8 \pm 1.8 \text{ cm}^{-1}$ in idler mode, and $26.0 \pm 1.3 \text{ cm}^{-1}$ in 1064 nm mode.

It is instructive to see the effect of the pulse bandwidth on the spectral resolution. Figure 5.11 compares two measurements of the same region of polystyrene, recorded in idler mode and 1064 nm mode. The two neighboring peaks at 1585 and 1603 cm⁻¹ are clearly resolvable in 1064 nm mode with its narrower CARS bandwidth, while the idler mode's broader bandwidth decreases the spectral resolving power to the point where the two peaks become one.

During CARS experiments using the Paladin laser, the OPO was found to have an optimum cavity length where the output power was high and the pulses were spectrally narrow. However, lengthening the OPO cavity relative to this optimum dramatically increased the detected CARS intensity, even though the output power was less than maximum and the pulses were slightly broader than the minimum. This odd detuning behavior was measured in idler mode on the 3055 cm⁻¹ line of polystyrene (see section 5.5) and is shown in figure 5.12.



Figure **5.12**. *Effect of detuning the cavity length on the OPO output intensity, spectral width, and CARS intensity. The solid lines are a guide to the eye. The intensities are shown on the leftmost vertical axis; the spectral width is shown on the right.*

5.5 CARS spectroscopy of several substances

CARS spectra of several substances were recorded from about 900–3600 cm⁻¹, using an automated data acquisition program written in LabVIEW. The values from the lock-in amplifier (section 4.5) were divided by the values from the idler photodiode and square of the values from the signal photodiode (section 4.4) and corrected for the photomultiplier sensitivity as a function of the anti-Stokes wavelength. This correction eliminates the $1/\lambda^2$ dependence of eq. (3.10), leaving a measurement value that is proportional to $|\chi^{(3)}|^2$.

The results presented here concern pure substances with well-known Raman spectra: a sample of bulk polystyrene cut from a CD jewel case; a sample of 99.9% pure toluene (Merck) contained between two microscope slide cover glasses, in a cell made from hole-punched cellophane tape; and finally a daub of superglue (poly(ethyl-2-cyanoacrylate), brand name Electrolube Cyanolube) on a glass microscope slide. The former two were chosen because of their phenyl groups, which exhibit strong Raman resonances around 1000 cm⁻¹, and the latter because of a strong Raman peak in the silent region (see figure 3.3) due to the cyano group. Figure 5.13 shows the structural formulae of these substances.



Figure **5.13***. Structural formulae of the substances used in the CARS spectroscopy experiments.*

Color in	Scanning	Filter	Poling	Raman	Alignment	Scanning
ingures	moue	set	(um)	(am^{-1})		range
			(µm)	(cm)	(()	(0)
green	idler	1	6.95	3100–3600	132	116–147
blue	idler	1	6.95	2624–3150	107	91–124
red	idler	3	6.90	1800–2624	102	87–124
turquoise	1064 nm	2	6.95	1500-1850	130	111–147
purple	1064 nm	2	6.95	1250-1550	102	90–120
orange	1064 nm	3	6.90	950-1325	102	87–124

Table 5.1. Scanning scheme for CARS spectroscopy. The Raman shift and temperature figures given here are approximate; they vary somewhat depending on how well the OPO is aligned.

A CARS spectrum from 950–3600 cm⁻¹ can be obtained in six scans, each one indicated by a different color in the figures. A typical scanning scheme is shown in table 5.1. Each scan takes roughly three minutes, as the crystal's maximum heating or cooling rate is 10 °C/min. Scanning deeper into the fingerprint region is limited by the detector's exponentially decreasing sensitivity to the required wavelengths, while the upper limit is set by the OPO's minimum signal wavelength.

While scanning, the signal wavelength, used to calculate the Raman shift, is measured by a spectrum analyzer with 100 ms integration time (see section 4.3) with a spectral resolution of 0.44 nm. However, the signal wavelength must be determined with greater accuracy, or the spectral resolution of the CARS measurements would be very low indeed: data points would be spaced by the large value of 9 cm⁻¹.

Since the signal spectrum is approximately Gaussian within the optimum scanning range, we used the center wavelength of a Gaussian curve fit to the spectrum analyzer's output. This way, we could avoid switching to a slower, higher-resolution spectrometer, which would have severely limited the scanning speed.

The CARS spectrum of polystyrene is shown in figure 5.14. The strong aromatic ring vibration around 1000 cm^{-1} is clearly visible, as is the C–H region from 2800–3100 cm⁻¹. There is a section missing from the silent region, as the OPO became misaligned during that measurement. Details of the spectrum, marked with the corresponding Raman shifts, are shown in figure 5.15. In general, the CARS intensity peak is at a slightly lower energy than the Raman shift, because of the resonant and non-resonant CARS contributions mixing (see section 3.6). An odd artifact, also occurring in toluene and several measurements of other substances not shown here, is visible in figure 5.14 at 2650 cm⁻¹.

Figure 5.16 shows the CARS spectrum of toluene. The details in figure 5.17 show it to be similar to the polystyrene spectrum; as figure 5.13 shows, the toluene molecule is similar to the repeating unit of polystyrene. The strange artifact encountered at 2650 cm^{-1} in polystyrene is also visible in toluene. Another unidentified peak occurs at 1660 cm^{-1} . Since water has a vibrational mode around that wavenumber, it may be caused by contamination with water.

Finally, the CARS spectrum of poly(ethyl-2-cyanoacrylate) is shown in figure 5.18. Here, there is no strong aromatic ring vibration in the fingerprint region, but the C–H region is clearly visible, and the C \equiv N vibration is evident in the middle of what is normally the silent region. All of the Raman lines listed in Edwards and Day [13], except for the very weak ones, are discernible in the spectrum; of special note are the lines caused by small amounts of unreacted monomeric ethyl-2-cyanoacrylate.

5.6 Removing the nonresonant background

In figures 5.14–5.19, the CARS peaks are slightly displaced from the known locations of the Raman resonances. This is due to the interference term between the nonresonant background and resonant CARS (3.14). If CARS spectra are to be put to good use in spectroscopy applications, then the nonresonant background must be removed.

The current experimental setup cannot measure the phase of the anti-Stokes beam relative to the pump beam. However, as discussed in section 3.8, we can retrieve the resonant CARS contribution, and therefore the proper locations of the molecular vibrations, from a CARS spectrum even without having measured the phase. We use the maximum entropy method of phase retrieval published by Vartiainen et al. [44], in an online application kindly made available by the AMOLF institute [3]. We



Figure 5.14. CARS spectrum of polystyrene. The colors indicate the various scanning modes and filter sets.



Figure 5.15. CARS spectrum of polystyrene (detail). The corresponding Raman shifts are indicated above the CARS peaks. The Raman shifts are from reference [42], except for those marked by *, which are from reference [45].



Figure 5.16. CARS spectrum of toluene. The colors indicate the various scanning modes and filter sets.



Figure **5.17**. *CARS* spectrum of toluene (detail). The corresponding Raman shifts are indicated above the CARS peaks. The Raman shifts are from reference [42], except for those marked by *, which are from a spontaneous Raman spectrum.



Figure 5.18. CARS spectrum of poly(ethyl-2-cyanoacrylate). The colors indicate the various scanning modes and filter sets.



Figure 5.19. CARS spectrum of poly(ethyl-2-cyanoacrylate) (detail). The corresponding Raman shifts [13] are indicated above the CARS peaks. Features due to unreacted monomeric ethyl-2-cyanoacrylate are indicated by *. The features at 3033, 3049, and 3129 cm⁻¹ are lost in the noise, but were present in a spontaneous Raman measurement of the same sample.

used the CARS spectrum of polystyrene (figure 5.14) as input to the program, after processing it with a central moving average 2.5 cm⁻¹ wide, since the algorithm does not perform particularly well on high-frequency noise.

The smoothed CARS spectrum, the processed Raman lineshapes extracted from it, and the spontaneous Raman spectrum of polystyrene are compared in figure 5.20. The lineshapes in the processed spectrum exhibit much more similarity to those in the spontaneous Raman spectrum, and are visible much more clearly.

The resonances at 1585 and 1603 cm⁻¹ are far less intense in the processed spectrum. This can be ascribed to spectral broadening of the OPO outputs. The resonance locations in the processed spectrum are 7 cm⁻¹ (corresponding to a signal wavelength difference of 0.44 nm) lower on average than their counterparts in the spontaneous Raman spectrum. This may be caused by a systematic error known to exist in the spectrum analyzer used to measure the signal wavelength. This error was thought to be 1.22 nm, but sufficient calibration data were not available and the actual error may be higher.

The phase extracted from the CARS data is shown in figure 5.21, together with the extracted Raman spectrum again for comparison.

5.7 CARS concentration measurements and dephasing

The O–H vibrations of water pose a problem in Raman spectroscopy, as they form a very broad agglomerate peak from about $3100-3550 \text{ cm}^{-1}$. However, in CARS, vibrational dephasing may reduce these problems. Dephasing is a quantum-mechanical effect, not explained in the present work's classical treatment of CARS. It is the phenomenon of an oscillator's energy leaking away through interactions with its environment. Dephasing times of vibrational states are often picoseconds in liquids and solids, and up to hundreds of picoseconds in gases [24], whereas the signal and idler pulses from the OPO are about half a picosecond. The O–H stretch vibration of water, on the other hand, has a dephasing time of about 90 fs [40], and the vibrational mode can thus relax to the ground state during the CARS interaction time.

We examined the 2850–3350 cm⁻¹ region of a sample of 99.9% pure ethanol and compared it to a sample of Koskenkorva Viina, a liquor made by diluting industrialgrade ethanol with spring water. It contains 38 vol% ethanol. A sample of distilled water was also included in the comparison. The samples were all the same thickness and all contained in a like manner.



Figure 5.20. Analysis of a CARS spectrum using the maximum entropy method [44, 3]. The original and processed CARS spectra are shown offset from the Raman spectrum for clarity.



Figure **5.21***. Raman intensity and anti-Stokes phase of the CARS spectrum of polystyrene, analyzed using the maximum entropy method* [44, 3]*.*



Figure **5.22.** *Spontaneous Raman spectra of* **99.9%** *pure ethanol*, *Koskenkorva Viina*, *and distilled water*.

In order to be able to compare the CARS intensities, which vary considerably between realignments of the OPO, the three samples were scanned in the same spectral region, without any delay or realignment between them, except to align the sample in the pump and Stokes beams' focus.

The spontaneous Raman spectra of these three samples are shown in figure 5.22. The water bands are clearly visible, starting around 3150 cm^{-1} . Ethanol's weak O–H vibration in that region is also visible on the pure ethanol sample.

The samples' CARS spectra are shown in figure 5.23. The water band is considerably weaker. It does not show up at all in the Raman spectrum calculated using phase retrieval, but that is because the complex Lorentzian model is classical. The O–H vibration in ethanol is also absent from the CARS spectrum, which may indicate that the dephasing time of ethanol's O–H stretch is also shorter than the temporal pulse length. However, no real conclusion can be reached without more detailed measurements; it may be that the vibration is simply too weak.

CARS spectroscopy can also be used for concentration measurements, as $|\chi^{(3)}|$ is proportional to the number of oscillators in the interaction volume. As a qualitative demonstration, we can use these data to verify the volume percentage of ethanol (i.e. alcohol percentage) of Koskenkorva Viina. The volume percentage *V* is equal



Figure **5.23**. *CARS* spectra of 99.9% pure ethanol, Koskenkorva Viina, and distilled water. The corresponding Raman shifts of ethanol are indicated above the CARS peaks, taken from reference [42].

to:

$$V = \frac{\rho_{\rm KV}}{\rho_{\rm ethanol}} C, \tag{5.6}$$

where ρ is the density and *C* is the ratio of molar concentrations of ethanol in the two samples, approximated by:

$$C = \frac{A_{\rm KV} - (1 - C)A_{\rm water}}{A_{\rm ethanol}} = \frac{A_{\rm KV} - A_{\rm water}}{A_{\rm ethanol} - A_{\rm water}}.$$
(5.7)

Here, *A* is the measured CARS intensity, proportional to $|\chi^{(3)}|$. The second expression in eq. (5.7) is produced by solving for *C*, but divides by zero if $A_{\text{water}} = A_{\text{ethanol}}$. At one point, the ethanol and water curves do cross in figure 5.23, but by excluding the range between 2950 to 3050 cm⁻¹ and averaging the rest, we obtain an alcohol percentage of $41.0\% \pm 5.3\%$ (standard deviation).
6

Conclusion and recommendations

The recommendations in this section are divided into two parts: trivial recommendations (section 6.2), for directly improving the results of this experiment; and future work (section 6.3), or suggestions for further research building upon these results.

6.1 Summary

In this research, the green-pumped, picosecond-pulsed optical parametric oscillator (OPO) described in Bouwmans [4], with a variable output coupler, using a magnesium oxide-doped periodically poled lithium niobate (MgO:PPLN) crystal as its gain medium, was rebuilt. The signal wavelength ranges from 880 to 1040 nm and the idler from 1090 to 1350 nm. The signal wavelength can be scanned continuously for sub-ranges on the order of 30 nm.

A qualitative theoretical model, based on the conversion efficiency model of Tukker [43] was developed to explain the curve shape of the total OPO output power as a function of the variable output coupler setting. We expect this model to be quantitatively accurate if the pump pulses' Gaussian temporal shape is taken into account.

Two different modes of coherent anti-Stokes Raman scattering (CARS) were demonstrated, one using the OPO's idler as the Stokes wavelength and the other using 1064 nm light as the Stokes wavelength. Both modes used the OPO's signal as the pump and probe wavelength. High-resolution CARS spectroscopy was demonstrated from 900 to 3600 cm⁻¹ in six steps and using three filter sets on three organic substances. The spectroscopic resolution was increased by using a Gaussian fitting algorithm on the spectrum of the OPO's signal.

The effects of sample concentration and input pulse bandwidth on the CARS intensity were tested. The vibrational dephasing of the O–H stretch vibration in water was also briefly investigated.

The phase retrieval algorithm using the maximum entropy method described in Vartiainen et al. [44] was used to compare the CARS spectra to known Raman spectra, which were in extremely good agreement.

6.2 Recommended improvements

The most important characteristics of CARS spectroscopy are spectroscopic range and sensitivity. The lowest Raman shift demonstrated in this research is 900 cm⁻¹, but the all-important fingerprint region extends down to 500 cm⁻¹. Therefore, for real applications of chemical selectivity, the spectral range must be improved. Sensitivity is also important for real applications, because the naturally-occurring concentrations of molecules, in the human body for example, are much lower than the high concentrations and pure samples imaged in this research. For example, the CARS signal of a 200 mM solution of L-phenylalanine was too weak to detect with the present setup.

The spectroscopic range is currently limited by the photomultiplier tube used to detect the anti-Stokes light from the sample. Its sensitivity to wavelengths longer than about 800 nm drops steeply. There are photomultipliers on the market that are sensitive to longer wavelengths; using one that is sensitive to at least 1000 nm would enable scanning to about 250 cm⁻¹, enough to cover any vibrations of interest.

Replacing the photomultiplier with one sensitive to at least 1040 nm would also allow the 1064 nm light to be used as the pump wavelength and the OPO's idler as the Stokes. This would allow scanning from 440–3700 cm⁻¹ with a simpler filtering scheme: only one filter set would be necessary, blocking wavelengths of 1064 nm and higher. By definition, the anti-Stokes wavelength would be the same as that of the OPO's signal, opening the door to phase-sensitive heterodyne detection [23]. It would also improve sensitivity, since the pump intensity (in which the CARS intensity is quadratic, eq. (3.10)) would not be limited by the OPO's maximum output, but rather by the sample's damage threshold.

In the same way, improving the OPO output power could also improve sensitivity, while still using the current CARS wavelength configurations. The output power is currently limited by the OPO pump power, which must keep below the surmised damage threshold of the nonlinear crystal's antireflection coating. This threshold is

not known with any certainty. A more aggressive approach to testing the damage threshold, could prove it to be higher, perhaps even much higher, than currently estimated. If the damage threshold is not much higher than now estimated, then removing the anti-reflection coating altogether may prove advantageous.

Pumping the OPO with the Vanguard laser produced spectrally narrower pulses: around 4 cm^{-1} instead of 26 cm⁻¹. Narrower pulses will improve the CARS sensitivity, as well as increase the spectral resolution (5.4). Cheng et al. [6] show that the nonresonant CARS contribution has a quadratic dependence on the spectral width, while the resonant contribution saturates at a certain spectral width. Evans and Xie [14] suggest that a bandwidth of $3-5 \text{ cm}^{-1}$ (pulse length 2–7 ps) is a good balance between peak signal strength and spectral resolution.

6.3 Future work

The apparatus described here could be made into an automated, self-contained spectroscopy system, with possible commercial applications. Currently, a user performing a scan must tune the cavity length to an appropriate value and align the OPO before beginning. The scan itself is completely automated. If the cavity length and OPO alignment could be computer-controlled, then the entire spectrum could be scanned automatically, only stopping to change the filter set. Using the 1064 nm and idler beams together would even eliminate the need to change the filters. Automating the OPO would entail placing one cavity mirror (M14 in figure 4.5), in a piezo-steered mirror mount, on a motorized translation stage [4, p. 38]. The sample holder, the retroreflectors for overlapping the pump and Stokes pulses in time, and the mirrors for overlapping them in space, would also need to be motorized.

Imaging using this setup is a matter of replacing the sample holder with a twodimensional piezo scanner. Combining this CARS system with a laser microscope would be especially advantageous, as detailed microscope imaging at any Raman shift in the fingerprint region would then be possible. Acquiring one entire spectrum per pixel would be prohibitively slow, but imaging at one frequency could be used to identify the areas in which the user wishes to measure the entire spectrum.

A useful application of this technology would be to image and identify proteins. The locations of proteins in a sample could be determined by imaging the sample at the frequency of the amide I band (1630–1700 cm⁻¹), characteristic of protein backbones. Having located the proteins, the vibrational fingerprint spectrum at one point could then be measured, yielding information about their identity and structure (for example, see the paper of Combs et al. on examining tryptophan side chains in proteins using vapor-phase Raman spectroscopy [9].)



Figure 6.1. Example of a 4f shaper configuration, so named because of its length of four times the lenses' focal length f. (Based on Sprünken [39, p. 6].)

Another possibility for future research, inspired by the focus-engineered CARS of Krishnamachari and Potma [25], is that of two-dimensional spatio-spectral amplitude shaping. Using a 4f shaper configuration (figure 6.1), a pulse can pass through a two-dimensional phase mask (static, or dynamic if using a device such as a spatial light modulator) that modulates the spatial amplitude in one direction and the spectral amplitude in another.

The author proposes to use two of these devices to split the pump and Stokes pulses in two around their center frequencies ω_p and ω_s , so that frequencies lower or higher than the center frequency end up on opposite spatial halves of the pulse. This can be achieved with a fairly simple amplitude mask, an example of which is shown in figure 6.2. By choosing the pulses' shapes carefully, the corresponding anti-Stokes frequency $\omega_{as} = 2\omega_p - \omega_s$ can be kept the same for both halves, while slightly separating the Raman shifts $\Omega = \omega_p - \omega_s$. The energy diagram of this CARS scheme is shown in figure 6.3.

The anti-Stokes beam then consists of two spatial halves with the same frequency, but resulting from two different Raman shifts. If the Raman shifts are around a vibrational resonance, then the two halves of the anti-Stokes beam will have differing amplitudes and phases. Beams such as these have well-known far-field intensity distributions [15, 8] which are functions of the amplitude and phase difference between the two halves, and thus the relative phase of the anti-Stokes beam can be measured directly without heterodyne detection.



Figure 6.2. A simple two-dimensional amplitude mask for CARS using spatio-spectral amplitude shaping.



Figure 6.3. Energy diagram of the proposed spatio-spectral amplitude-shaped CARS.



A.1 Physical quantities in vacuum

In order to avoid confusion between the values of a physical quantity, such as wavelength, in vacuum and in a medium, the symbol for the value in vacuum will always be denoted with the subscript 0. For example, ε is the permittivity of the medium in question, while ε_0 is the permittivity of free space. Exceptions to this rule are w_0 , which is used to denote the radius of a Gaussian laser beam at its waist, and z_0 , which is the conventional symbol for the Rayleigh range, always an optical path length.

A.2 Various mathematical conventions

Vectors (**v**) are set in bold type. Their magnitudes are set in italics (*v*). Single components of a vector will be indicated with a subscript (v_x, v_y, v_z) . The unit vector of a particular vector is denoted by a hat ($\hat{\mathbf{v}} = \mathbf{v}/v$). The imaginary unit for complex numbers, $\sqrt{-1}$, is denoted by *i*.

The convolution of two functions is denoted by *:

$$(f*g)(x) = \int_{-\infty}^{\infty} f(\xi)g(x-\xi)\,d\xi. \tag{A.1}$$

The sinc function is defined as:

$$\operatorname{sinc} x = \frac{\sin x}{x}.$$
 (A.2)

The shah function is defined as:

$$\operatorname{III}(t) = \sum_{n = -\infty}^{\infty} \delta(t - n), \tag{A.3}$$

where δ is the Dirac delta function:

$$\delta(x) = \begin{cases} \infty, & x = 0, \\ 0, & \text{otherwise,} \end{cases}$$
(A.4)

so that:

$$\int_{-\infty}^{\infty} \delta(x) \, dx = 1. \tag{A.5}$$

A.3 Symbols and constants

Symbol	Meaning	Value
Co	velocity of light in vacuum	299792458 m/s
е	Euler's number	2.71828182846
h	Planck's constant	$6.62606896 imes 10^{-34} \text{ J} \cdot \text{s}$
ħ	Dirac's constant	$h/2\pi$
k_B	Boltzmann's constant	$1.3806504 \times 10^{-23} \text{ J/K}$
ε_0	permittivity of free space	$8.85418781762 imes 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2$
μ_0	permeability of free space	$4\pi imes 10^{-7}~{ m N/A^2}$
π	pi	3.14159265359

 Table A.1. Table of physical and mathematical constants.

Symbol	Meaning
Α	frequency-independent amplitude
В	magnetic field
С	phase velocity of light
D	electric displacement
d	distance
Ε	electric field
f	focal length; frequency
8	degeneracy
Н	auxiliary field
(Continued on next page)	

Symbol	Meaning
Ι	intensity
k	wave vector
$\Delta \mathbf{k}$	phase mismatch
Κ	spring constant
k	wave number (propagation)
L,l	length
Μ	magnetization
п	index of refraction
Р	polarization
Р	power
R	reflection coefficient; radius of curvature
r	position
Т	temperature; transmission coefficient
t	time
w	beam radius
z_0	Rayleigh range
Δ	angular frequency detuning
ε	permittivity
η	conversion efficiency
θ	angle
κ	coupling constant
Λ	poling period
λ	wavelength
μ	permeability
$\tilde{\mathcal{V}}$	wavenumber (spectroscopy)
ρ	density
ϕ	photon flux density
χ	susceptibility
Ω	Raman shift
ω	angular frequency

(Continued from previous page)

Table A.2. Table of symbols.

B

Derivations of useful expressions

This appendix collects three derivations that the author considers useful, and would like to have had available, for the purpose of understanding the subject matter in this thesis.

B.1 The coupled wave equations

Here, we will derive three-dimensional coupled wave equations and conservation laws for the process of optical parametric amplification, closely following the method of Svelto [41, pp. 514–7].

Note that the substitution $k_i = n_i \omega_i / c$, mentioned at the top of p. 516 of Svelto, is incorrect: *c*, used there to mean the phase velocity of light, should be c_0 , as in eq. (B.7).

The propagation equation in a second-order nonlinear medium can be derived easily from (2.7):

$$\nabla^2 \mathbf{E} = \frac{1 + \chi^{(1)}}{c_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{\chi^{(2)}}{c_0^2} \frac{\partial^2 \mathbf{E}^2}{\partial t^2}.$$
 (B.1)

The electric field $\mathbf{E}(\mathbf{r}, t)$ and its complex amplitude $E(\mathbf{r})$ will be written here without their time and position arguments. Now we consider an incident wave of three frequencies ω_s , ω_i , and $\omega_p = \omega_s + \omega_i$, corresponding to the signal, idler, and pump

waves which are explained in section 2.4. We will assume that the propagation equation holds separately for each frequency component of the wave:

$$\nabla^2(\mathbf{E})_j = \frac{1+\chi^{(1)}}{c_0^2} \frac{\partial^2(\mathbf{E})_j}{\partial t^2} + \frac{\chi^{(2)}}{c_0^2} \frac{\partial^2(\mathbf{E}^2)_j}{\partial t^2},\tag{B.2}$$

where $(\mathbf{E})_j$, etc. denotes the component of the wave with frequency ω_j . These components can be written in the forms:

$$(\mathbf{E})_j \propto E_j e^{i(\omega_j t - \mathbf{k}_j \cdot \mathbf{r})},$$
 (B.3)

$$(\mathbf{E}^2)_j \propto (E_{NL})_j e^{i(\omega_j t - \mathbf{k}_j \cdot \mathbf{r})},$$
 (B.4)

where E_{NL} is shorthand for the complex amplitude of the nonlinear part of the electric field.

Inserting (B.3) and (B.4) into (B.2) yields:

$$\nabla^2 E_j - 2i\mathbf{k}_j \cdot \nabla E_j - |\mathbf{k}_j|^2 E_j = -\frac{\omega_j^2 (1 + \chi^{(1)})}{c_0^2} E_j - \frac{\omega_j^2 \chi^{(2)}}{c_0^2} (E_{NL})_j.$$
(B.5)

Then, applying the slowly varying wave approximation:

$$\nabla^2 E_j \ll \mathbf{k}_j \cdot \nabla E_j,\tag{B.6}$$

and noting that:

$$k_j = n_j \omega_j / c_0, \tag{B.7}$$

and:

$$1 + \chi^{(1)} = \varepsilon / \varepsilon_0 \approx n_i^2, \tag{B.8}$$

yields the differential equation

$$\hat{\mathbf{k}}_j \cdot \nabla E_j = -\frac{1}{2} i \frac{\omega_j \chi^{(2)}}{n_j c_0} (E_{NL})_j.$$
(B.9)

The reader should note that $\hat{\mathbf{k}}$ is the *unit* wave vector, pointing in the direction of propagation, and equal to \mathbf{k}/k .

Recalling (2.14), our incident wave is written as:

$$\mathbf{E}(\mathbf{r},t) \propto E_p e^{i(\omega_p t - \mathbf{k}_p \cdot \mathbf{r})} + E_s e^{i(\omega_s t - \mathbf{k}_s \cdot \mathbf{r})} + E_i e^{i(\omega_i t - \mathbf{k}_i \cdot \mathbf{r})} + \text{c.c.}$$
(B.10)

Squaring (B.10) and a considerable amount of algebra and perseverance will yield the entire gamut of second-order three-wave mixing processes. Since we are only interested in the components at ω_p , ω_s , and ω_i , we ignore the rest:

Now we can calculate the components of the nonlinear complex amplitude E_{NL} for the pump, signal, and idler frequencies from (B.4):

$$(E_{NL})_{p} = 2E_{s}E_{i}e^{i(\mathbf{k}_{s}+\mathbf{k}_{i}-\mathbf{k}_{p})\cdot\mathbf{r}},$$

$$(E_{NL})_{s} = 2E_{p}E_{i}^{*}e^{i(\mathbf{k}_{p}-\mathbf{k}_{i}-\mathbf{k}_{s})\cdot\mathbf{r}},$$

$$(E_{NL})_{i} = 2E_{p}E_{s}^{*}e^{i(\mathbf{k}_{p}-\mathbf{k}_{s}-\mathbf{k}_{i})\cdot\mathbf{r}}.$$

$$(B.12)$$

This allows us to derive a field equation in the form of (B.9) for each frequency, representing the magnitude of $\chi^{(2)}$ by the effective nonlinear coefficient χ_{eff} :

$$\begin{aligned}
\hat{\mathbf{k}}_{p} \cdot \nabla E_{p} &= -i \frac{\omega_{p} \chi_{\text{eff}}}{n_{p} c_{0}} E_{s} E_{i} e^{-i(\Delta \mathbf{k}) \cdot \mathbf{r}}, \\
\hat{\mathbf{k}}_{s} \cdot \nabla E_{s} &= -i \frac{\omega_{s} \chi_{\text{eff}}}{n_{s} c_{0}} E_{p} E_{i}^{*} e^{i(\Delta \mathbf{k}) \cdot \mathbf{r}}, \\
\hat{\mathbf{k}}_{i} \cdot \nabla E_{i} &= -i \frac{\omega_{i} \chi_{\text{eff}}}{n_{i} c_{0}} E_{p} E_{s}^{*} e^{i(\Delta \mathbf{k}) \cdot \mathbf{r}},
\end{aligned}$$
(B.13)

where the phase mismatch $\Delta \mathbf{k} = \mathbf{k}_p - \mathbf{k}_s - \mathbf{k}_i$.

We now introduce the frequency-independent amplitude A_j :

$$A_j = E_j \sqrt{\frac{n_j}{\omega_j}}.$$
(B.14)

As Svelto points out [41, p. 517], this will become convenient when deriving the Manley-Rowe relations (section B.2), since it allows us to eliminate ω_j . Eqs. (B.13) then become the coupled wave equations:

$$\begin{aligned}
\hat{\mathbf{k}}_{p} \cdot \nabla A_{p} &= -i\kappa A_{s}A_{i}e^{-i(\Delta \mathbf{k}) \cdot \mathbf{r}}, \\
\hat{\mathbf{k}}_{s} \cdot \nabla A_{s} &= -i\kappa A_{p}A_{i}^{*}e^{i(\Delta \mathbf{k}) \cdot \mathbf{r}}, \\
\hat{\mathbf{k}}_{i} \cdot \nabla A_{i} &= -i\kappa A_{p}A_{s}^{*}e^{i(\Delta \mathbf{k}) \cdot \mathbf{r}},
\end{aligned}$$
(B.15)

where the coupling parameter κ is shorthand for

$$\kappa = \frac{\chi_{\text{eff}}}{c_0} \sqrt{\frac{\omega_p \omega_s \omega_i}{n_p n_s n_i}}.$$
(B.16)

B.2 The Manley-Rowe relations

Multiplying eqs. (B.15) by A_p^* , A_s^* , and A_i^* respectively, and comparing the results, we obtain:

$$(\hat{\mathbf{k}}_s \cdot \nabla A_s) A_s^* = (\hat{\mathbf{k}}_i \cdot \nabla A_i) A_i^* = -(\hat{\mathbf{k}}_p \cdot \nabla A_p^*) A_p.$$
(B.17)

To get rid of the dot products, we can define r_j as the position along each axis of propagation $\hat{\mathbf{k}}_j$. Also, we consider that the photon flux density of the wave is:

$$\phi_j = \frac{I_j}{\hbar\omega_j} = \frac{\varepsilon_0 c_0}{2\hbar} |A_j|^2. \tag{B.18}$$

Note that the photon flux density is proportional to $|A_j|^2$ with a proportionality constant independent of the medium.

Subsequently, adding (B.17) to its complex conjugate and inserting (B.18) yields the Manley-Rowe relations (see section 2.4):

$$\frac{\partial \phi_s}{\partial r_s} = \frac{\partial \phi_i}{\partial r_i} = -\frac{\partial \phi_p}{\partial r_p}.$$
(B.19)

B.3 The quasi-phase-matched idler intensity

Eq. (2.21) is not sufficient to describe the behaviour of quasi-phase matching in a nonlinear crystal. In order to obtain an analytical expression for the idler intensity throughout a periodically poled crystal, we must return to eq. (2.15) and once again assume constant I_p and I_s , but replace Δk by a position-dependent phase mismatch representing the periodic poling repeating every coherence length l_c :

$$\Delta k_r(r) = \begin{cases} \Delta k, & 0 \le r \le l_c, \ 2l_c < r \le 3l_c, \ \dots \\ -\Delta k, & l_c < r \le 2l_c, \ 3l_c < r \le 4l_c, \ \dots \end{cases}$$
(B.20)

The idler field equation then becomes:

$$\frac{dA_i}{dr} = -i\kappa A_p A_s^* e^{ir\Delta k_r(r)},\tag{B.21}$$

and assuming as before that $A_i(0) = 0$:

$$A_{i}(L_{c}) = -i\kappa A_{p}A_{s}^{*}\int_{0}^{L_{c}} e^{ir\Delta k_{r}(r)} dr.$$
 (B.22)

Transforming this into a piecewise integral over intervals of length l_c yields:

$$A_i(L_c) = -i\kappa A_p A_s^* \left(\sum_{p=0}^{N-1} \int_{pl_c}^{(p+1)l_c} e^{(-1)^p ir\Delta k} \, dr + (-1)^N \int_{Nl_c}^{L_c} e^{(-1)^N ir\Delta k} \, dr, \right)$$
(B.23)

where *N* is the largest integer that satisfies $Nl_c \leq L_c$.

Integrating the above and rearranging the terms of the sum yields:

$$A_{i}(L_{c}) = -\frac{\kappa A_{p}A_{s}^{*}}{\Delta k} \left(\sum_{p=0}^{N-1} (-1)^{p} \left(e^{i(p+1)l_{c}\Delta k} + e^{-i(p+1)l_{c}\Delta k} \right) + (-1)^{N} e^{(-1)^{N}iL_{c}\Delta k} - 1 \right).$$
(B.24)

Using a well-known trigonometric identity, we can say:

$$(-1)^{p} \left(e^{i(p+1)l_{c}\Delta k} + e^{-i(p+1)l_{c}\Delta k} \right) = 2(-1)^{p-1}\cos(p+1)l_{c}\Delta k, \tag{B.25}$$

and, since the definition of the coherence length (2.23) states that $l_c \Delta k = \pi$:

$$2(-1)^{p}\cos(p+1)l_{c}\Delta k = 2(-1)^{p}\cos(p+1)\pi$$

$$= 2(-1)^{p}(-1)^{p+1}$$

$$= -2.$$
(B.26)

Meanwhile, we will consider the other term separately for both cases of N being odd and even. If N is even:

$$e^{iL_{c}\Delta k} - 1 = (e^{iL_{c}\Delta k} - 1)e^{-iL_{c}\Delta k/2}e^{iL_{c}\Delta k/2}$$

$$= (e^{iL_{c}\Delta k/2} - e^{-iL_{c}\Delta k/2})e^{iL_{c}\Delta k/2}$$

$$= 2ie^{iL_{c}\Delta k/2} \sin L_{c}\Delta k/2.$$
(B.27)

If *N* is odd,

$$-e^{-iL_{c}\Delta k} - 1 = -(e^{-iL_{c}\Delta k} - 1) - 2$$

$$= 2ie^{-iL_{c}\Delta k/2} \sin L_{c}\Delta k/2 - 2,$$
(B.28)

in the same way.

By way of eqs. (B.26), (B.27), and (B.28), eq. (B.24) becomes:

$$A_i(L_c) = -\frac{\kappa A_p A_s^*}{\Delta k} \left(2ie^{(-1)^N i L_c \Delta k/2} \sin L_c \Delta k/2 - (2N+1) + (-1)^N \right).$$
(B.29)

The intensity is then given by:

$$I_{i} = \frac{8\omega_{i}^{2}I_{p}I_{s}(\chi^{(2)})^{2}}{n_{p}n_{s}n_{i}\varepsilon_{0}c_{0}^{3}(\Delta k)^{2}}\left((-1)^{N}(2N+1)\sin^{2}L_{c}\Delta k/2 + (N+\frac{1}{2}(1-(-1)^{N}))^{2}\right),$$
(B.30)

where, again, *N* is the largest integer that satisfies $Nl_c \leq L_c$, or perhaps more elegantly:

$$N = \left\lfloor \frac{L_c}{l_c} \right\rfloor. \tag{B.31}$$

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C

Specifications of the components used in the experiments

C.1 OPO cavity mirrors

The cavity mirrors are custom-coated plano-concave lenses and flat windows from CVI Laser Optics LLC. Their specifications are listed in table C.1.

The anti-reflection coating on the front side is shown in figure C.1. The coating on the back side is R < 1% for 1080–1300 nm at 2°. The front coating was specifically measured to be $R = 0.99888 \pm 0.00001$, or OD 2.95, for 980 nm at 0°.

C.2 Nonlinear crystal

The nonlinear crystal from HC Photonics Corp. is made of 5 mol% magnesium oxide-doped lithium niobate (MgO:LiNbO₃). It is 20 mm along the optical axis, 7 mm wide, and 0.5 mm high. It contains six domains with different poling periods: $6.80 \mu m$, $6.85 \mu m$, $6.90 \mu m$, $6.95 \mu m$, $8.36 \mu m$, and $10.00 \mu m$.

The end faces of the crystal carry an anti-reflection coating which is shown in figure C.2.

Lithium niobate's index of refraction is about 2.2, but in order to calculate the wavelengths that satisfy the phase matching condition, far more precision is required. The index of refraction varies with the temperature and the incident light's



Figure C.1. Custom coating of the OPO cavity mirrors.



Figure C.2. Custom coating of the nonlinear crystal end faces.

	Curved mirrors	Flat mirrors
Diameter	25.4 mm	id.
Diameter tolerance	+0.00 mm, -0.25 mm	id.
Thickness	3.9 mm (centre), 4.2 mm (edge)	6.35 mm
Thickness tolerance	$\pm 0.25 \text{ mm}$	id.
Focal length	-500.0 mm (nominal),	—
	-495.7 mm (at 532 nm),	
	−508.3 mm (at 1064 nm)	
Focal length tolerance	$\pm 0.5\%$	—
Radius of curvature	257.5 mm	—
Substrate material	BK7 glass	id.
Surface figure	$\lambda/10$ at 633 nm	id.
Surface quality	10-5 laser quality	id.
Chamfer	$0.35~\mathrm{mm}$ at 45°	id.
Clear aperture	Exceeds central 85% of dimension	id.
Concentricity	$\leq 0.05 \text{ mm}$	
Wedge	—	$\leq 0^\circ \; 5'$

Table C.1. Specifications of the cavity mirrors.

wavelength. The temperature-dependent Sellmeier equation of MgO:LiNbO₃, with which the index of refraction can be calculated, is [26]:

$$n_e^2 = a_1 + b_1 f(T) + \frac{a_2 + b_2 f(T)}{\lambda_0^2 - (a_3 + b_3 f(T))^2} + \frac{a_4 + b_4 f(T)}{\lambda_0^2 - a_5^2} - a_6 \lambda_0^2, \tag{C.1}$$

where:

$$f(T) = (T - 24.5 \,^{\circ}\text{C})(T + 570.82 \,^{\circ}\text{C}). \tag{C.2}$$

The parameters a_n and b_n are given in table C.2. Note that eq. (C.1) yields the index of refraction for rays parallel to the axis of anisotropy (extraordinary rays); all the wavelengths must be in micrometers.

Eq. (2.24), when expressed in terms of the vacuum wavelength, is:

$$\frac{1}{\Lambda} = \frac{n_p(\lambda_p, T)}{\lambda_p} - \frac{n_s(\lambda_s, T)}{\lambda_s} - \frac{n_i(\lambda_i, T)}{\lambda_i}.$$
 (C.3)

This allows us to calculate a temperature tuning curve for the signal and idler wavelengths in different poling periods. HC Photonics also supplied tuning data for the crystal, which is shown in table C.3. Fitting the temperature tuning curve to the HC Photonics data yields the following correction:

$$\Lambda_{\text{corrected}} = (1.0087 - 5.93 \times 10^{-5} \ ^{\circ}\text{C}^{-1} T)\Lambda. \tag{C.4}$$

Parameter	Value
<i>a</i> ₁	5.5336
<i>a</i> ₂	0.100473 μm ²
<i>a</i> ₃	0.20692 μm
a_4	100 μm ²
a_5	11.34927 μm
<i>a</i> ₆	$1.5334 imes 10^{-2} \ \mu m^{-2}$
b_1	$4.629 imes 10^{-7}$ °C ²
b_2	$3.862 \times 10^{-8} \ \mu m^2 \cdot \ ^{\circ}C^{-2}$
b_3	$-0.89 \times 10^{-8} \ \mu m \cdot \ ^{\circ}C^{-2}$
b_4	$2.657 \times 10^{-5} \ \mu m^2 \cdot \ ^\circ C^{-2}$

Table C.2. Parameters of the temperature-dependent Sellmeier equation for 5 mol% magnesium oxide-doped lithium niobate [26].

Wavelength	Poling	period	(µm) at t	emperature
	25 °C	50 °C	100 °C	160 °C
650 nm	10.19	10.13	10	9.84
720 nm	8.52	8.47	8.36	8.21
900 nm	7.15	7.1	7.01	6.88
970 nm	7.01	6.97	6.87	6.74
1040 nm	6.96	6.92	6.82	6.7

Table C.3. Tuning data from HC Photonics for different signal wavelengths and crystal temperatures in 5 mol% *magnesium oxide-doped lithium niobate* [4, p. 45].

C.3 Oven and temperature controller

The crystal is mounted inside a modified Thorlabs PV20 oven with a built-in Platinum Thermistor 100 Ω temperature sensor. A Thorlabs TC200 temperature controller controls the oven. The controller can be set to a certain temperature (T_{set}) from 20–205 °C in steps of 0.1 °C, and the temperature from the sensor (T_{act}) can be read out, also to an accuracy of 0.1 °C. The controller includes a feedback regulation system, but this was found to be inaccurate by measuring the temperature inside the oven with two thermocouples [4, p. 46]. The systematic difference ΔT between the temperature measured by the thermocouples and the temperature inside the lithium niobate crystal was determined from the temperature tuning curve (fig. 5.1) and was found to be approximately 10 °C. The real temperature can be calculated from either T_{set} or T_{act} [4, p. 46]:

$$T \approx 9.81 \times 10^{-5} T_{\text{set}}^2 + 0.921 T_{\text{set}} - 4.87 - \Delta T,$$
 (C.5)

$$T \approx 6.41 \times 10^{-5} T_{\rm act}^2 + 0.952 T_{\rm act} - 2.95 - \Delta T.$$
 (C.6)

It was found that these equations only apply if the temperature controller's maximum allowed power is set to 18.0 W.

C.4 Laser

During assembly and testing of the OPO, the pump light was emitted by a Spectra Physics Vanguard 2000-HM532, a mode-locked Nd:YVO₄ laser delivering second-harmonic pulses. It was later replaced by a similar, but higher output power, Coherent Paladin Nd:YVO₄ laser modified to emit second-harmonic pulses instead of third. Both lasers' relevant specifications are listed in table C.4. Both lasers also emitted their leftover 1064 nm light from a separate aperture, although that of the Vanguard was never used in these experiments.

	Vanguard	Paladin
Wavelength	532 nm	id.
Power	2 W	> 9.5 W
Repetition rate	80 MHz	$80\pm1~MHz$
Pulse width	< 12 ps	> 15 ps at 1064 nm
Mode	TEM_{00}	id.
M^2 quality factor	< 1.3	< 1.2
Divergence	< 1 mrad	< 550 µrad
Beam diameter	1.4 mm at $1/e^2$ intensity	$1 \text{ mm} \pm 15\%$
Pointing stability	$< 25 \mu rad / ^{\circ}C$	$<$ 20 µrad/ $^{\circ}$ C
Beam ellipticity	< 1.2	0.9–1.1
Average power stability	< 2%	$\pm 2\%$
Amplitude noise	< 1% rms, 10 Hz to 2 MHz	id.
Polarization ratio	< 100:1 vertical	id.

Table C.4. Specifications of the Vanguard and Paladin lasers.

C.5 Other components

Component	Туре	Specifications	
BRF	birefringent filter	Coherent dye laser Lyot filter	
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Component	Туре	Specifications
CCD	camera	Philips black & white CCD camera
СН	chopper	Thorlabs мс1000А, 10-slot blade
CM1, 2	curved mirror	see section C.1
F1	filter	colored glass longpass filter, $\lambda_c \approx 630$ nm
F2	filter	Thorlabs ND01B neutral density filter,
		optical density 0.1
F3	filter	Schott RG610 longpass filter,
		$\lambda_c = 610 \pm 6 \; \mathrm{nm}$
F4	filter	Schott NG9, $d = 4.3$ mm, optical density
		5.0
F5	filter	Schott RG780 longpass filter,
		$\lambda_c = 780 \pm 9 \text{ nm}$
F 6	filter	Phila Optics Inc. RG17 longpass filter,
		$\lambda_c \approx 695 \text{ nm}$
F7	filter	colored glass longpass filter, $\lambda_c \approx 630$ nm
F8	filter	Thorlabs ND20A neutral density filter,
		optical density 2.0
F9	filter	Phila Optics Inc. IRG1 longpass filter,
		$\lambda_c pprox 920 \text{ nm}$
F10, 11	filter	Chroma нq1000sP shortpass filter,
		$\lambda_c = 1000 \ \mathrm{nm}$
F12, 13	filter	Chroma нq750sp-2p shortpass filter,
		$\lambda_c = 750 \text{ nm}$
F14	filter	3RD Millennium 3RD580LP longpass filter,
		$\lambda_c = 580 \pm 3 \text{ nm}$
F15, 16	filter	Chroma нq825/150м-2P bandpass filter,
		$\lambda = 750900 \text{ nm}$
F17	filter	Thorlabs FES0850 shortpass filter,
		$\lambda_c = 850 \text{ nm}$
FC	fiber coupler	see L6
GP	glass plate	generic brand microscope cover slip,
		$24 \times 60 \text{ mm}$
GTP1, 2	Glan-Taylor	Thorlabs
	polarizer	
HWP1, 2	half-wave plate	Thorlabs wpнo5м-532, $\lambda=$ 532 nm
нwр3	half-wave plate	Thorlabs wpнo5м-1064, $\lambda=1064$ nm
нwр4-7	half-wave plate	Thorlabs анwро5м-950,
		$\lambda = 6901200 \text{ nm}$
11–5	iris	—

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Component	Туре	Specifications
L1	lens	f = -75 mm, uncoated
L2	lens	f = 100 mm, uncoated
l3, 4	lens	Thorlabs la1509-b, $f = 100$ mm, AR
		750–1100 nm
L5	lens	f = 125 mm, uncoated
l6	lens	Thorlabs f220SMA-b, $f = 11.0$ mm, AR
		750–1100 nm
l7, 9	lens	f = 50 mm, uncoated
l8	lens	Thorlabs LA1433-C, $f = 150$ mm, AR
		1100–1600 nm
LASER1	laser	Spectra Physics Vanguard 2000-нм532,
		see section C.4
LASER2	laser	Coherent Paladin (modified), see
		section C.4
M1-4	mirror	Thorlabs вв1-ео2, HR 400–750 nm
М5	mirror	HR 532 nm
мб, 25, 29–30	mirror	Thorlabs PF10-03-P01, reflective at
		500–2000 nm
M7–10, 15–24, 27	mirror	Thorlabs вв1-еоз, HR 750–1100 nm
M11–12	curved mirror	see section C.1
м13–14, 28	mirror	see section C.1
м26	mirror	dichroic mirror, HR 530–1000 nm
NLC	nonlinear crystal	see section C.2
OI1	optical isolator	AR 532 nm
OI2	optical isolator	AR 1064 nm
OL1	objective lens	Nachet PL-FL $40 \times$ infrared-corrected
		objective, $NA = 0.60$, $f = 5$ mm, working
		distance 3 mm, AR 800–1600 nm
OL2	objective lens	Nikon M-Plan $40 imes$ super-long working
		distance brightfield objective, $NA = 0.40$,
		working distance 14.9 mm
PBC1	polarizing	AR 1064 nm
	beamsplitter	
PBC2	polarizing	AR 890–1040 nm
	beamsplitter	
PD1	photodiode	silicon photodiode, $\lambda = 190-1100$ nm
PD2	photodiode	Roithner LaserTechnik GmbH PT611,
	Ĩ	InGaAs photodiode, $\lambda = 800-2600$ nm
		1

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Component	Туре	Specifications
PMT	photomultiplier	Hamamatsu H6780-20, $\lambda=$ 300–900 nm
	tube	
RR1, 2	retroreflector	Thorlabs PS972
SA	spectrum	Ocean Optics Inc. HR2000
	analyzer	
WLM	wavelength	Coherent WaveMate
	meter	

Table C.5. Specifications of the components used in the setup. AR stands for anti-reflection coating, HR for highly reflective coating, and λ_c denotes the cutoff wavelength of an edgepass filter.

Bibliography

- Armstrong, J. A., Bloembergen, N., Ducuing, J., & Pershan, P. S. (1962). Interactions between light waves in a nonlinear dielectric. *Physical Review*, 127(6), 1918–1939.
- [2] Bjorkholm, J. (1971). Some effects of spatially nonuniform pumping in pulsed optical parametric oscillators. *IEEE Journal of Quantum Electronics*, 7(3), 109– 118.
- [3] Bonn, M., & Vartiainen, E. M. (n.d.). Maximum entropy method for phase retrieval of CARS data. Online software application. Retrieved July 23, 2008 from http: //memcars.amolf.nl.
- [4] Bouwmans, H. S. P. (2006). A green pumped OPO for highly sensitive molecular detection using CARS. Master's thesis, Universiteit Twente.
- [5] Boyd, R. W. (2003). Nonlinear optics. Academic Press, second ed.
- [6] Cheng, J.-X., Volkmer, A., Book, L. D., & Xie, X. S. (2001). An epi-detected coherent anti-Stokes Raman scattering (E-CARS) microscope with high spectral resolution and high sensitivity. *Journal of Physical Chemistry B*, 105(7), 1277– 1280.
- [7] Cheng, J.-X., & Xie, X. S. (2004). Coherent anti-Stokes Raman scattering microscopy: Instrumentation, theory, and applications. *Journal of Physical Chemistry B*, 108(3), 827–840.
- [8] Chimento, P. F. (2008). Orbital angular momentum mode analysis with a micro mirror array. Universiteit Leiden.
- [9] Combs, A., McCann, K., Autrey, D., Laane, J., Overman, S. A., & Thomas, G. J., Jr. (2005). Raman signature of the non-hydrogen-bonded tryptophan side chain in proteins: experimental and ab initio spectra of 3-methylindole in the gas phase. *Journal of Molecular Structure*, 735–736, 271–278.
- [10] Ebrahimzadeh, M., & Dunn, M. H. (2000). Optical parametric oscillators. In M. Bass (Ed.) *Handbook of Optics*, vol. 4, chap. 22, (pp. 22.1–22.72). McGraw-Hill.
- [11] Eckbreth, A. C. (1978). BOXCARS: crossed-beam phase-matched CARS generation in gases. *Applied Physics Letters*, 32(7), 421–423.

- [12] Eckbreth, A. C., Dobbs, G. M., Stufflebeam, J. H., & Tellex, P. A. (1984). CARS temperature and species measurements in augmented jet engine exhausts. *Applied Optics*, 23(9), 1328–1339.
- [13] Edwards, H. G. M., & Day, J. S. (2004). Fourier transform Raman spectroscopic studies of the curing of cyanoacrylate glue. *Journal of Raman Spectroscopy*, 35, 555–560.
- [14] Evans, C. L., & Xie, X. S. (2008). Coherent anti-Stokes Raman scattering microscopy: chemical imaging for biology and medicine. *Annual Review of Analytical Chemistry*, 1, 883–909.
- [15] Gao, Z., & Lü, B. (2007). Phase-flipped Hermite-Gaussian beams and their propagation beyond the paraxial approximation. *Optics Communications*, 279, 130–140.
- [16] Garbacik, E. T. (2008). *Measuring coherent anti-Stokes Raman scattering using an optical parametric oscillator*. Bachelor's thesis, Lawrence University/Universiteit Twente.
- [17] Gerry, C. C., & Knight, P. L. (2005). Introductory quantum optics. Cambridge University Press.
- [18] Giordmaine, J. A., & Miller, R. C. (1965). Tunable coherent parametric oscillation in LiNbO₃ at optical frequencies. *Physical Review Letters*, 14(24), 973–976.
- [19] Griffiths, D. J. (1999). Introduction to electrodynamics. Prentice Hall, third ed.
- [20] Hellwarth, R. W. (1979). Third-order optical susceptibilities of liquids and solids. *Progress in Quantum Electronics*, 5, 1–68.
- [21] Jurna, M. (2005). High-power continuous-wave optical parametric oscillator for spectroscopy and gas detection. Institut de Ciències Fotòniques, Castelldefels, Spain.
- [22] Jurna, M. (2006). *CARS microscopy based on a green pumped OPO*. Master's thesis, Universiteit Twente.
- [23] Jurna, M., Korterik, J. P., Otto, C., Herek, J. L., & Offerhaus, H. L. (2008). Background free CARS imaging by phase sensitive heterodyne CARS. In preparation, accepted to Optics Express.
- [24] Kamga, F. M., & Sceats, M. G. (1980). Pulse-sequenced coherent anti-Stokes Raman scattering spectroscopy: a method for suppression of the nonresonant background. *Optics Letters*, 5(3), 126–128.
- [25] Krishnamachari, V. V., & Potma, E. O. (2008). Detecting lateral interfaces with focus-engineered coherent anti-Stokes Raman scattering microscopy. *Journal of Raman Spectroscopy*, 39, 593–598.

- [26] Li, H. P., Tang, D. Y., Ng, S. P., & Kong, J. (2006). Temperature-tunable nanosecond optical parametric oscillator based on periodically poled MgO:LiNbO₃. *Optics & Laser Technology*, 38, 192–195.
- [27] Lotem, H., Lynch, R. T., Jr., & Bloembergen, N. (1976). Interference between Raman resonances in four-wave difference mixing. *Physical Review A*, 14(5), 1748–1755.
- [28] Maker, P. D., & Terhune, R. W. (1965). Study of optical effects due to an induced polarization third order in the electric field strength. *Physical Review*, 137(3A), A801–A818.
- [29] Myers, L. E., Eckardt, R. C., Fejer, M. M., Byer, R. L., Bosenberg, W. R., & Pierce, J. W. (1995). Quasi-phase-matched optical parametric oscillators in bulk periodically poled LiNbO₃. *Journal of the Optical Society of America B*, 12(11), 2102–2116.
- [30] Paschotta, R. (2008). "Quasi-phase matching" Encyclopedia of Laser Physics and Technology. Retrieved July 14, 2008 from http://www.rp-photonics.com/ quasi_phase_matching.html.
- [31] Raman, C. V., & Krishnan, K. S. (1928). A new type of secondary radiation. *Nature*, 121(3048), 501–502.
- [32] Saleh, B. E. A., & Teich, M. C. (1991). *Fundamentals of photonics*. John Wiley & Sons.
- [33] Samoc, A. (2003). Dispersion of refractive properties of solvents: Chloroform, toluene, benzene, and carbon disulfide in ultraviolet, visible, and nearinfrared. *Journal of Applied Physics*, 94(9), 6167–6174.
- [34] Schott AG (2001). Optical glass data sheets. Schott AG.
- [35] Shirley, J. A., Hall, R. J., & Eckbreth, A. C. (1980). Folded BOXCARS for rotational Raman studies. *Optics Letters*, 5(9), 380–382.
- [36] Smekal, A. (1923). Zur Quantentheorie der Dispersion. *Naturwissenschaften*, 11(43), 873–875.
- [37] Smith, E., & Dent, G. (2005). *Modern Raman spectroscopy: a practical approach*. John Wiley & Sons.
- [38] Sneep, M., & Ubachs, W. (2005). Direct measurement of the Rayleigh scattering cross section in various gases. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 92(3), 293–310.
- [39] Sprünken, D. P. (2008). *A 2D spatial light modulator for spatio-temporal shaping*. Master's thesis, Universiteit Twente.

- [40] Stenger, J., Madsen, D., Hamm, P., Nibbering, E. T. J., & Elsaesser, T. (2001). Ultrafast vibrational dephasing of liquid water. *Physical Review Letters*, 87(2), 027401.
- [41] Svelto, O. (1998). *Principles of lasers*. Springer, fourth ed. Trans. David C. Hanna.
- [42] Tanabe, K., & Hiraishi, J. (n.d.). Spectral database for organic compounds. National Institute of Advanced Industrial Science and Technology, Japan. Retrieved July 23, 2008, from http://riodb01.ibase.aist.go.jp/sdbs.
- [43] Tukker, T. W. (1998). *A high repetition rate picosecond infrared light source for a sum-frequency vibration spectrometer*. Ph.D. thesis, Universiteit Twente.
- [44] Vartiainen, E. M., Rinia, H. A., Müller, M., & Bonn, M. (2006). Direct extraction of Raman line-shapes from congested CARS spectra. *Optics Express*, 14(8), 3622–3630.
- [45] Xie, X. S., & Offerhaus, H. L. (2006). *Polystyrene spontaneous Raman*, 532 nm *excitation*. Measured at CARS workshop, Xie group (unpublished).
- [46] Zumbusch, A., Holtom, G. R., & Xie, X. S. (1999). Three-dimensional vibrational imaging by coherent anti-Stokes Raman scattering. *Physical Review Letters*, 82(20), 4142–4145.

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This is characteristic of my attitude towards my physics studies. Two years ago, disillusioned by a number of uninspired courses taught using bad PowerPoint slides, all I wanted was to get it over with and become a starving comic strip artist, or perhaps a columnist for Skeptic magazine, or both; and now here I am, investigating the PhD programs of various graduate schools. After experiencing real research in the Optical Sciences group, as well as a three-month internship at the University of Leiden, I enjoy physics as much as I did when I decided to study it, fresh from high school, although hopefully for different and more mature reasons.

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